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FINAL REPORT

**SPACE STATION
MOLECULAR SIEVE
DEVELOPMENT
Contract No.
NAS8-36424**

**86-30002
May 1, 1986**

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Prepared for

**NASA Marshall Space Flight Center
Huntsville, Alabama**



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**Craig Chang
Signal Research Center**

**Jean Rousseau
AIRsearch Manufacturing Company**

Prepared for

**NASA Marshall Space Flight Center
Huntsville, Alabama**



AIRESEARCH MANUFACTURING COMPANY

FOREWORD

This report documents a six-month effort aimed at the development of hydrophobic sorbent for CO₂ removal from space cabin atmosphere. The program was funded by the NASA Marshall Space Flight Center, Alabama, under contract No. NA58-36424. Mr. Stephen P. Beale was the contracting officer, and Ms. Theresa Geiger was the technical monitor.

AiResearch Manufacturing Company of Los Angeles, Ca. was the contractor to the NASA; Mr. Jean Rousseau was the principal investigator. The sorbent development effort was conducted at the Signal Research Center, Des Plaines, Illinois. This organization is a sister company of AiResearch through the Signal Conglomerate. Dr. Craig Chang of the Signal Research Center was responsible for all activities involved with development and characterization of the sorbent. AiResearch responsibility was concerned with the conduct of the overall program and system evaluation.



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SECTION 1

INTRODUCTION AND SUMMARY

INTRODUCTION

An essential function of a space environmental control system is the removal of carbon dioxide (CO₂) from the atmosphere to control the partial pressure of this gas at levels lower than 3 mm Hg. The use of regenerable solid adsorbents for this purpose has been demonstrated effective and reliable during the Skylab mission. The process involves selective concentration of carbon dioxide at the surface of a microporous solid (adsorbent) and release of the adsorbed gas by increasing temperature and/or reducing the partial pressure of CO₂ in the gas phase.

Earlier sorbent systems used zeolite molecular sieves. These inorganic solids typically are hydrophilic in nature, and low relative humidity in air reduces drastically the capacity for CO₂ removal. A separate bed for the control of moisture is necessary in order to use the zeolite material effectively for CO₂ removal. The Skylab system was such; regeneration was effected by exposing the sorbent bed to the vacuum of space and dumping water vapor as well as CO₂ overboard.

For long duration missions it may be desirable to concentrate the carbon dioxide for processing and oxygen recovery. Additionally, non-venting operational requirements on the space station preclude the use of a Skylab-type system.

Carbon, especially molecular sieve carbon, represents a hydrophobic class of adsorbent. Many thermosetting polymers have been found to produce carbon molecular sieves upon pyrolysis. Carbon molecular sieves are composed of small crystallites of carbon with trigonal bonding. These crystallites are cross-linked to form a disordered cavity-aperture structure. The apertures are believed to be slit-shaped and the size of the slits can be altered, depending on the polymer precursor and heat treatment temperature among other variables.

Carbon molecular sieve is a novel, hydrophobic adsorbent with excellent potential for space station application. Although carbon molecular sieves have been synthesized and investigated, these sieves have been designed to simulate the sieving properties of 5A zeolite and for O₂/N₂ separation.

This program was designed to develop hydrophobic carbon molecular sieves for CO₂ removal from a space station crew environment. It is a first phase effort involved in sorbent material development and in demonstrating the utility of such a material for CO₂ removal on space station.

PROGRAM OBJECTIVES

The major objective of the proposed program was to design a carbon molecular sieve material that incorporates the following features:

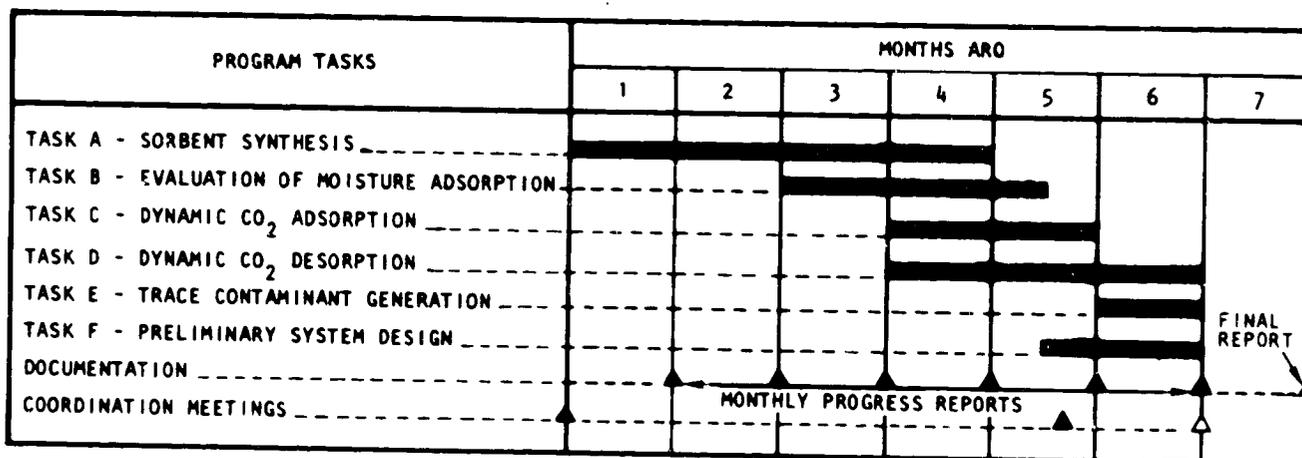


- (a) it is hydrophobic
- (b) it has high dynamic capacity for carbon dioxide at the low partial pressure of the space station atmosphere
- (c) it is chemically stable and will not generate contaminants

Another objective was to demonstrate the utility of this novel sorbent for space station carbon dioxide removal by comparing a carbon molecular sieve system with other approaches currently considered for this ECLSS function.

PROGRAM SCOPE

The program covered a 6-month period. The kickoff meeting was held at the NASA Marshall Space Flight Center on June 11, 1985. Program tasks are listed in the schedule of Figure 1-1.



NOTE: DARKENED BARS AND TRIANGLES INDICATE COMPLETED TASKS.

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Figure 1-1. Program Schedule

ACHIEVEMENTS

All program tasks have been completed and the objectives have been met. The sorbent materials developed have been demonstrated to adsorb and desorb carbon dioxide with only minimal reduction due to the presence of water. Sufficient data were generated to support preliminary design studies which show conclusively that significant benefits could be realized through the use of these sorbents for CO₂ removal on space station.

Major program accomplishments are listed below:

- (a) More than 90 sorbents have been prepared to produce 40 different carbon molecular sieves from 8 different types of polymer precursors. Among these adsorbents, 33 have been found to adsorb CO₂ selectively at a CO₂ partial pressure of 0.4 kPa (0.4 percent in air).
- (b) These carbon molecular sieves have been found to be selective for CO₂ over moisture. Water adsorption at less than 50 percent relative humidity is essentially negligible. Adsorption of water is very slow and the amount of adsorption at relative humidities higher than 50 percent is strongly affected by the preparation condition.
- (c) Five polymer precursors have been identified as promising starting materials for the preparation of carbon molecular sieves. Among them, the polyvinylidene chloride-polyvinyl chloride copolymer produces carbons with the highest CO₂ capacity. The formulation of this polymer is critical in the preparation of the carbon adsorbent. A polyvinylidene chloride homopolymer appears to be the best substitute, but yields reduced capacity.
- (d) Carbon molecular sieves have been found to desorb CO₂ at temperature significantly lower than 5A zeolite.
- (e) A combination of petroleum asphaltene and sulfite pulp waste liquor has been found to be adequate for binding molecular sieve carbon. It has been established that 12 percent binder will provide adequate mechanical strength for the adsorbent pellets.
- (f) Limited dynamic breakthrough tests showed that the binder was not adsorbing CO₂.
- (g) Gas collected at 200°C from dynamic breakthrough tests has been analyzed for possible trace contaminants. Results showed no detectable contaminants at a detection limit of 10 ppm.
- (h) CO₂ capacities of the most promising carbon adsorbents have been measured. The capacities of the pure sorbent material (without binder) range from 0.013 to 0.033 g/g at a CO₂ partial pressure of 0.5 kPa.



- (i) A sorbent was selected for further characterization. This sorbent (CCSD-6) was prepared from polyvinylidene chloride-polyvinyl chloride copolymer. Equilibrium data were generated at room temperature and at temperatures that may be suitable for desorption (80 and 106°C).
- (j) A 2-bed regenerable CO₂ removal system using the selected CCSD-6 sorbent was modeled using computer techniques available from the Skylab program.
- (k) Parametric performance data were generated covering a range of internal operating parameters. These data are believed to yield conservative estimates of system weight and power.
- (l) The 2-bed carbon molecular sieve system was compared to three current competing techniques for CO₂ removal of space station:
 - 4-bed zeolite molecular sieve system
 - Solid amine water desorbed system (SAWD)
 - Electrodepolarized cell (EDC)

RESULTS

Isotherms for the selected sorbent are shown in Figure 1-2. For purposes of comparison, the capacity of zeolite 5A is also shown. The carbon sorbent is much more sensitive to temperature than the zeolite; the working capacity achievable is more than twice that of the competing zeolite. Further, desorption will occur at much lower temperature.

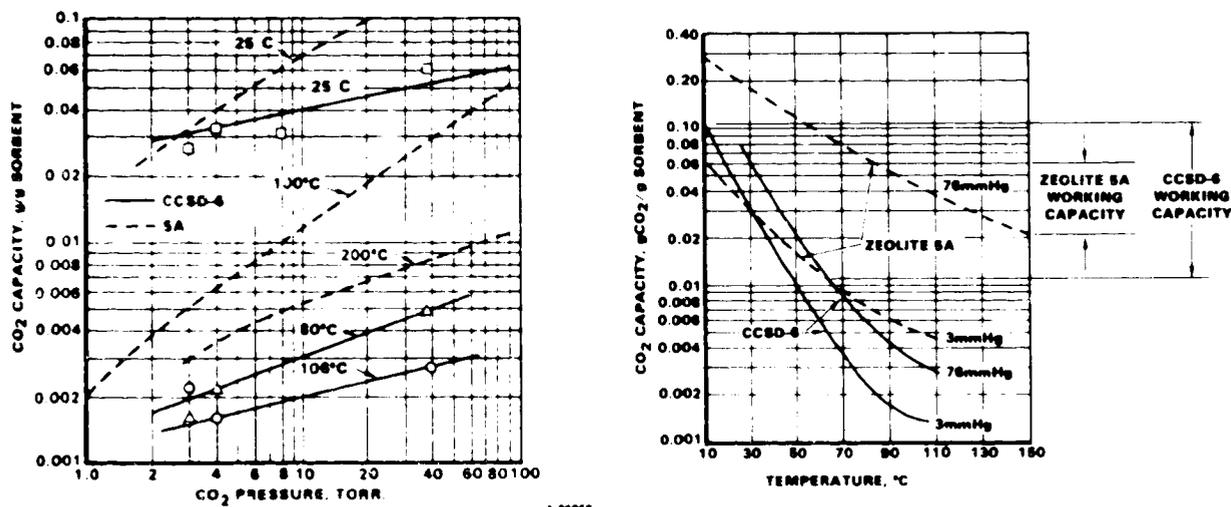
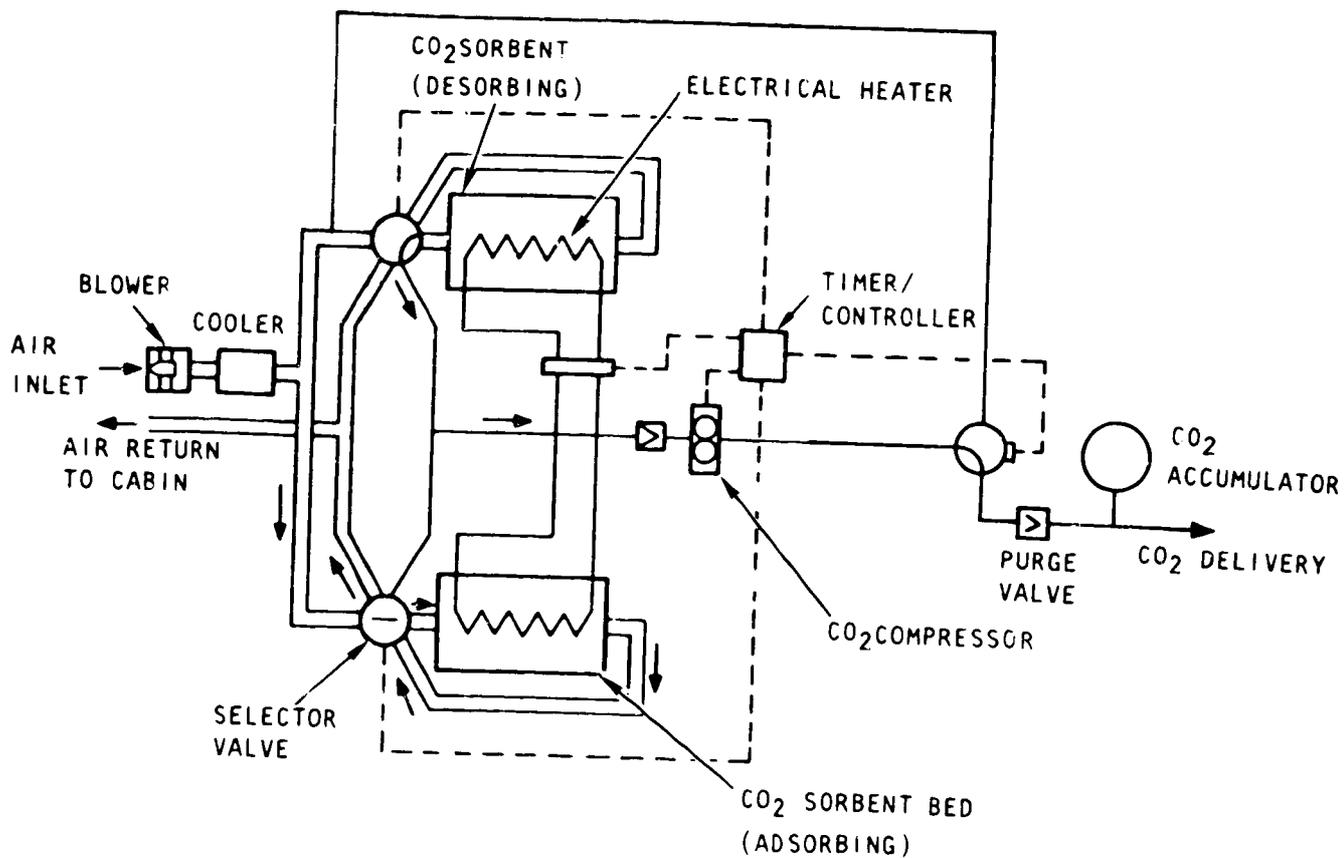


Figure 1-2. CCSD-6 CO₂ Capacity



A schematic of the 2-bed system characterized is shown in Figure 1-3. The sorbent is contained within the passages of plate fin heat exchanger. Thermal energy for desorption is provided by electrical heaters sandwiched between the plate fin passages. While one bed is adsorbing, the other is being desorbed. The adsorption and desorption times are the same. Upon valve switching, the air contained in the desorbing bed (ullage and adsorbed O_2/N_2) will be purged to the subsystem inlet for a short time.



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Figure 1-3. System Schematic

Pertinent system characteristics are presented in Table 1-1 for conditions corresponding to the space station cabin atmosphere. The data are for a 3-man system.

Table 1-2 compares the weight and power of the 2-bed carbon molecular sieve system with those of competing approaches. The data are self-explanatory and show the significant advantages afforded by the 2-bed system over these other CO_2 removal concepts.

TABLE 1-1.

SYSTEM CHARACTERISTICS
 CABIN TOTAL PRESSURE: 14.7 PSIA
 CABIN PCO₂: 3MM HG
 CO₂ REMOVAL RATE: 0.28 LB/HR

Half Cycle Time, min	45	60
CO ₂ Sorbent, kg	3.5	4.8
Desorption Temp., °C	74	74
Airflow, kg/min	0.43	0.39
System Wt, kg	44.1	48.1
Heater Power, w	81	92
Total Power, w	216	230

TABLE 1-2

COMPARISON OF APPROACHES

	2-Bed CCSD-6	4-Bed Zeolite	EDC	SAWD
Weight, kg	48	88	76	99
Volume, m ³	0.26	0.33	0.27	0.35
Power, w	230	535	344	511

RECOMMENDATIONS

To realize the advantages of the carbon molecular sieve system, it is recommended that this program be continued to:

- (a) complete the sorbent development effort and
- (b) demonstrate system performance prior to prototype development

Sufficient data were developed under the present program to support with a high degree of confidence the system level data generated and the conclusions reached. The work remaining in the area of sorbent development involves:



- (a) Sorbent optimization in terms of CO₂ capacity
- (b) Sorbent characterization to support system design and demonstrate durability
- (c) Development of pilot plant production procedures.

These tasks are relatively well defined and do not entail major technological problems.

The development of a demonstration system is also a straightforward endeavor; for this program, it is suggested that available RCRS hardware be used. The sorbent bed electrical heaters and controller have been identified as long lead time items that could be derived from available RCRS packages.

It is estimated that the go forward program could be completed in nine months, including sorbent and system development.

After careful consideration of the technical achievements of the sorbent development program and of the tasks remaining for complete demonstration, it is recommended that the 2-bed regenerable molecular sieve system be selected as baseline for the space station initial ECLSS configuration.



SECTION 2
SORBENT DEVELOPMENT

OF FOUR

INTRODUCTION

This section describes the approaches and the techniques used in preparation and characterization of the sorbents. Essential properties (CO₂ capacity and hydrophobicity) were considered in evaluating the various sorbents prepared. One formulation was selected for more detailed characterization to permit preliminary development of system parameters and comparison with other CO₂ removal approaches presently considered for space station.

The selected sorbent may not be optimal in terms of preparation and/or properties due to the limited scope of the program. However, sufficient data were generated to clearly demonstrate the significant advantages that could be realized through the use of carbon molecular sieves.

SORBENT SYNTHESIS

Two synthesis methods are generally available for the preparation of carbon molecular sieves: modification of an existing carbon adsorbent, and controlled carbonization of organic polymers. In this study, all carbon sieves were prepared through controlled carbonization process since this method generally produces carbons with the desired pore size distribution and uniform surface properties. The sorbent synthesis program including starting materials, preparation procedures, and screening tests is summarized in Figure 2-1.

- **STARTING MATERIALS**
 - THERMAL SETTING POLYMERS CONTAINING NO OXYGENS:
 - POLYVINYLIDENE CHLORIDE (PVDC),
 - POLYACRYLONITRILE (AN),
 - COPOLYMERS
- **PREPARATION PROCEDURES**
 - CARBONIZATION (600-1,200°C)
 - BINDING AND SHAPING
 - FINAL HEAT TREATMENT AND SURFACE MODIFICATION
- **SCREENING TESTS**
 - CO₂ ADSORPTION/DESORPTION
 - HYDROPHOBICITY

CARBONIZATION UNIT

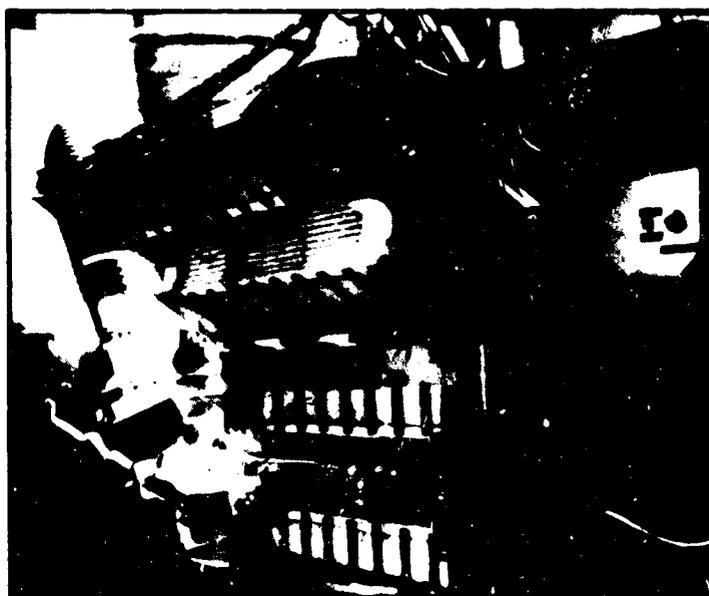


Figure 2-1. Sorbent Synthesis Program Summary

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The carbonization process was performed in a tube furnace (Figure 2-2) with a programmed heating rate. About 10 to 15 grams of a polymer precursor were heated in a 1-in. ID quartz tube placed in a furnace. After a steady stream of nitrogen (N₂) or helium (He) at a flow rate of 150 mL/min was introduced into the quartz tube for a least 30 min, the heating was started. The temperature of the furnace was increased at a constant rate from room temperature to the final temperature. For most of the carbon molecular sieves prepared in this study, a heating rate of 110°C/hr was used, and the final temperature was maintained for 1 1/2 hr before the product carbon was cooled to room temperature. The heating rate and the carbonization soaking time were varied with some preparations to study the effect of these preparation variables on the performance of the carbon molecular sieve. Final temperatures between 450 and 1,200°C were chosen for the preparation of carbon molecular sieves.

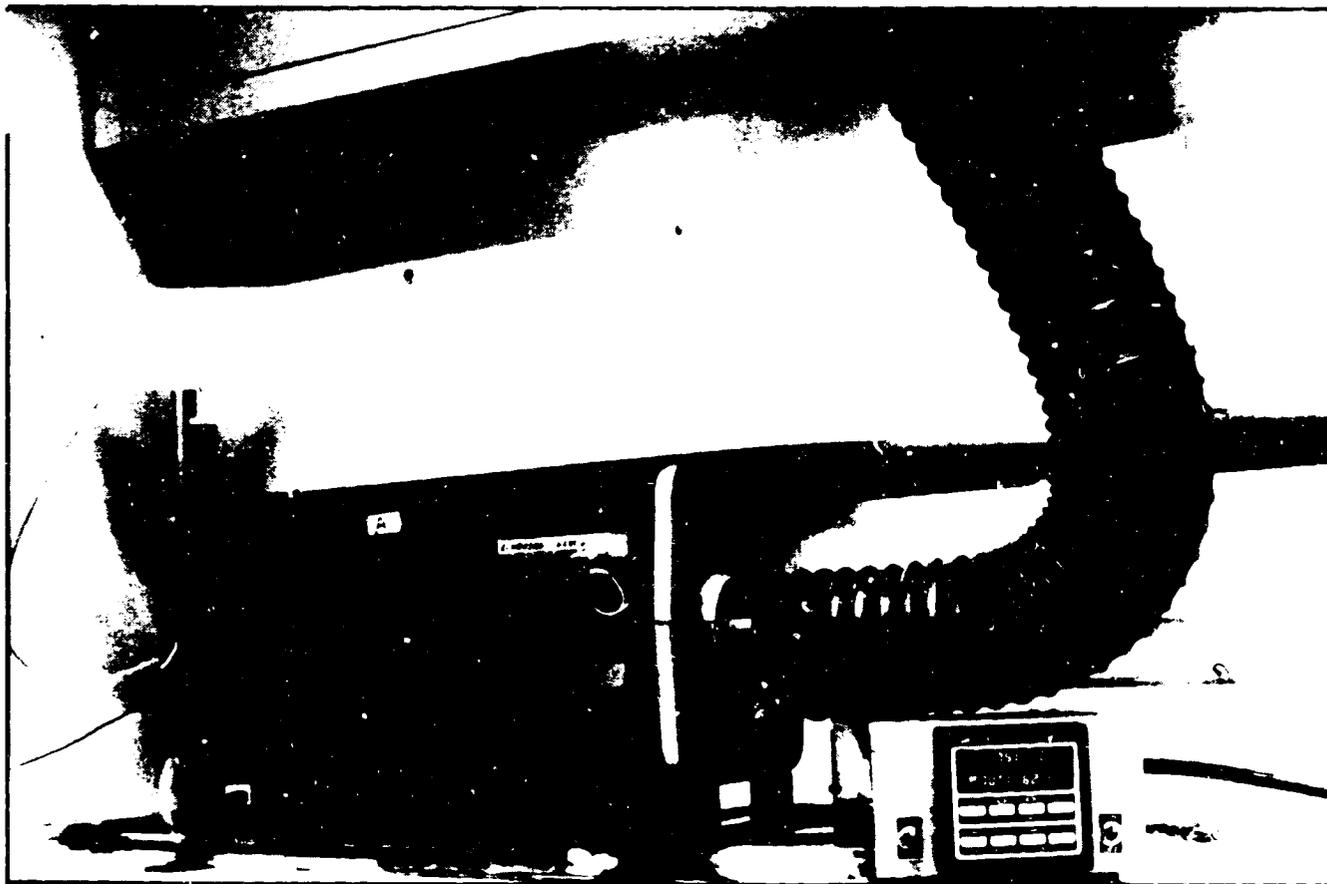


Figure 2-2. Laboratory Sorbent Preparation Furnace

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A number of polymer precursors were chosen for the preparation of carbon molecular sieves:

- (a) Polyvinylidene fluoride (PVDF)
- (b) Polyacrylonitrile (AN)
- (c) Polyvinylidene chloride (PVDC)
- (d) Polyvinylidene chloride - polyvinyl chloride (PVC) copolymers (Saran)



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- (e) Polyvinylidene chloride - acrylonitrile copolymers
- (f) Polystyrene (PS) - divinylbenzene (DVB) copolymers
- (g) Polychlorotrifluoroethylene (HALAR)

These polymers were chosen because they offer the best possibility of forming desirable adsorbents for the selective removal of CO₂ from the space station atmosphere. Polyvinylidene chloride was prepared from its monomer at 70°C with 2,2'-azobisisobutyronitrile as initiator. Other precursors were obtained from various chemical manufacturers and supply houses. They were used for controlled carbonization without further treatment.

Depending on the chemical nature of the polymer, a carbon product of 15 to 35 wt. percent was obtained in the preparation. The carbon molecular sieve obtained was ground and sieved to 40 to 70 U.S. mesh sizes for the evaluation by gas-solid chromatographic method. The same particle sizes were employed for the measurement of CO₂ capacity and water adsorption with a McBain balance. Some carbon sieve material was pulverized to 100 to 200 mesh sizes. They were bound with various binders and pelletized for dynamic adsorption/desorption studies.

The binding and shaping of the carbon molecular sieve were investigated with carbon binders. Attempts to bind the carbon sieve powder with polymer precursors resulted in mechanically weak pellets. Successful binding was obtained with a combination of asphaltene and sulfite waste liquor. Pulverized carbon molecular sieves were mixed with pulverized asphaltene and sulfite waste liquor. Asphaltene was prepared from a Kuwait crude with heptane as the solvent. The sulfite liquor contained 20.1 percent of dissolved solids. The weight ratio between asphaltene and the total solids in the sulfite liquor was kept at about 2. In addition, the weight ratios between the carbon molecular sieve and the binder materials were varied from a binder content of 10 to 20 wt. percent.

The mixture (carbon molecular sieve and the binder materials) was cold pressed with a Corver press at 5000 psi on a 6.4 mm die. Bound adsorbents were then heated in a tube furnace under N₂ atmosphere at 700°C for about 75 minutes.

In addition to the carbon molecular sieves prepared in this study, a number of adsorbents were also evaluated for the CO₂ removal from air. These adsorbents include 5A zeolite, dealuminated Y-faujasites, silicalite-1, and several molecular sieve carbons commercially available. 5A zeolite was chosen for comparison with the carbon molecular sieves prepared. Other zeolites were investigated as prospective hydrophobic adsorbents. Some properties and sources of these adsorbents are summarized in Table 2-1.

Sorbent Screening and Characterization

During this study, three characterization methods were employed to compare various sorbent and to assess the effects of preparation variables on CO₂ adsorption/desorption behavior, hydrophobicity, and surface properties of

TABLE 2-1
 COMMERCIAL ADSORBENTS EVALUATED FOR CO₂ REMOVAL

Commercial Sorbent	Nature of Sorbent	Si/AL	Source
5A Zeolite	Ca-A Zeolite	1	Union Carbide
USY-6	Dealuminated Y-Faujasite	7	Toyo Soda
USY-10	Dealuminated Y-Faujasite	63	Toyo Soda
Silicalite-1	All Silica Zeolite	-	Union Carbide
HGR-805	Carbon Sieve 5A	-	Takada
Carbosphere	Carbon Sieve	-	Altech
Carbosieve S-II	Carbon Sieve	-	Supelco
Carbosieve G	Carbon Sieve	-	Supelco

the material. These methods include gas-solid chromatograph (GC) analysis, gravimetric McBain balance, and dynamic adsorption/desorption bed (see Table 2-2). The gas-solid chromatographic method is a quick and effective method for screening the sorbent materials for CO₂ selectivity, CO₂ adsorption/desorption characteristics and hydrophobicity. McBain balance is a quantitative device for measuring equilibrium capacities for CO₂ and water. Dynamic adsorption/desorption bed provides breakthrough data for CO₂ adsorption and desorption, and cyclic characteristics of the adsorbent.

TABLE 2-2
 EVALUATION TECHNIQUES

Technique	Parameters Evaluated
Gas-Solid Chromatograph (GC) Analysis	CO ₂ Adsorption Hydrophobicity
Gravimetric McBain Balance	CO ₂ Capacity H ₂ O Capacity
Dynamic Adsorption/Desorption Bed	Coadsorption Breakthrough Data Cyclic Behavior

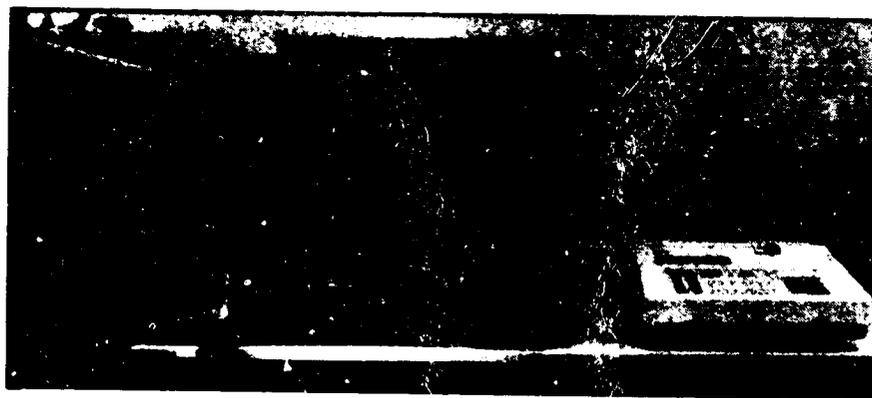
Gas-Solid Chromatographic Analysis

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The gas-solid chromatographic system used in the present study (Figure 2-3) is a Hewlett-Packard 5890A gas chromatographic unit equipped with thermal conductivity detector. The column is stainless steel tubing with a 1.85-mm ID and has an adsorbent volume of 1.5 ml. Adsorbents with particle sizes ranging from 0.21 to 0.42 mm diameters were packed into the column with maximum packing density possible. A vibrator was used to achieve the optimum packing.

After the column is packed with the adsorbent material, it is connected to the gas handling system and the conductivity detector in the gas chromatographic unit. The temperature of the adsorbent material is controlled in an oven.

The principle of the gas-solid chromatograph evaluation of adsorbents for the selective removal of CO₂ is illustrated in Figure 2-4. As shown in the top drawing of the figure, an inert gas (He) is introduced into the sorbent column continuously at a flow rate of about 20.0 mL/min, which corresponds to gas hourly space velocity (GHSV) of 800. At a constant sorbent temperature, and after a constant baseline signal is achieved at the detector, a known volume of a sample gas is introduced. The volume is controlled by a sampling valve on the chromatographic unit, or by a precision gas syringe. The sample gas is then followed by a continuous flow of He.



- GAS-SOLID CHROMATOGRAPHIC (GC) ANALYSIS:
 - HEWLETT-PACKARD 5890A G.C. UNIT,
 - 2MM STAINLESS STEEL COLUMN,
 - LENGTH-TO-AREA RATIO (L/A) = 2100;
 - GAS HOURLY SPACE VELOCITY (GHSV) - 800
 - FEED GAS - 0.01 - 0.1 mL
 - 0.4 TO 5% CO₂ IN AIR
- CARBON MOLECULAR SIEVES
 - PARTICLE DIAMETER: 0.21 - 0.42 mm
 - TOTAL VOLUME = 1.5 mL
 - ADSORBENT TEMPERATURE: 32 TO 200°C
- ZEOLITE 5A USED AS REFERENCE

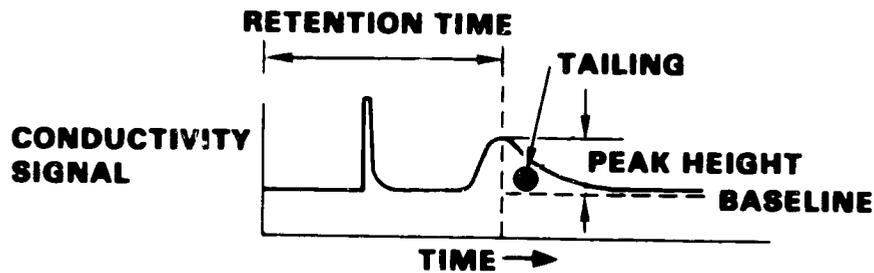
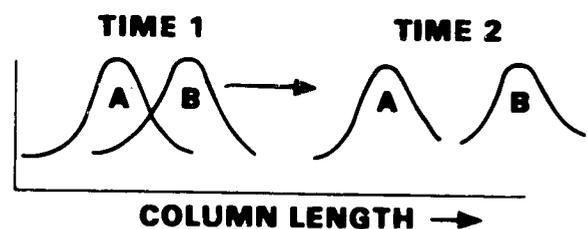
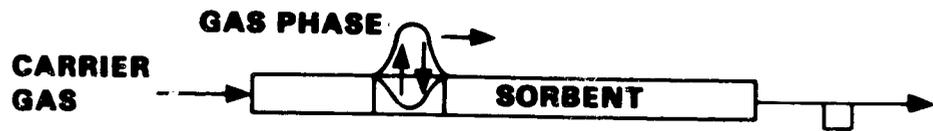
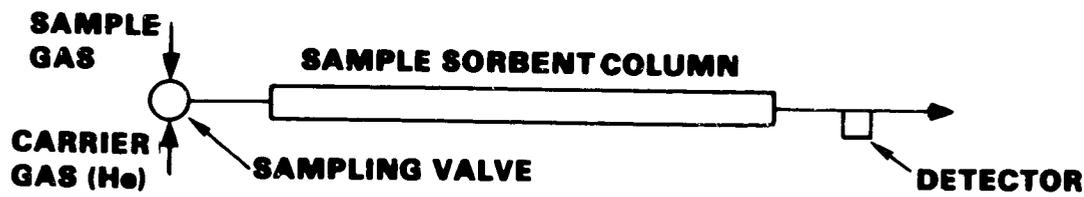
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Figure 2-3. Gas-Solid Chromatographic System



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- RETENTION TIME → {
 - RELATIVE SELECTIVITY
 - ADSORBENT HETEROGENEITY
 - ADSORBENT/ADSORBATE INTERACTION

- ELUTION PROFILE → {
 - ADSORPTION ISOTHERMS
 - HEAT OF ADSORPTION

- TEMPERATURE EFFECTS

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Figure 2-4. Gas-Solid Chromatographic Technique

In the column, the sample gas (say, CO₂) will distribute itself between the adsorbent phase (adsorption) and the gas phase while He gas is moving toward the end of the adsorbent column. Depending on the sorbent density, adsorption capacity, temperature, He flow rate, and other variables, the sample gas will move to the end of column at a characteristic flow rate. For a mixture of two gases on an adsorbent that adsorbs more strongly A than B (see Figure 2-4), B will move faster than A toward the downstream end of the column. A and B will thus separate along the adsorbent column length.

For a detector located at the end of the adsorbent column, gas peaks are detected as a function of the gas elution time. The retention time of a gas peak is the time between the injection of the sample and the moment when the majority of the gas is eluted from the column and detected. The retention time of a specific gas on an adsorbent and the elution profile of the gas provide information on the relative selectivity of the adsorbent toward the sample gas, the adsorbent/adsorbate interaction, the adsorbent heterogeneity, and adsorption isotherms. The effect of temperature on retention time is determined by the heat of adsorption of the sorbent material.

In the present investigation, CO₂ gases at concentrations from 0.4 to 100 percent in air were used to evaluate the CO₂ selectivities of sorbent materials at temperatures ranging from 32 to 200°C. During these studies, the adsorbent material was kept dry by introducing dry He carrier gas in the adsorbent column.

The effect of moisture on the CO₂ adsorption of the sorbent material was also determined in the gas-solid chromatographic system. For this study, He carrier gas was saturated with water by passing it through a water bath maintained at 24°C before injection into the adsorbent column. The decrease in the CO₂ retention time with the addition of moisture reflects the competitive adsorption between water and CO₂ under coadsorption conditions. Zeolite 5A was used as a baseline for comparison.

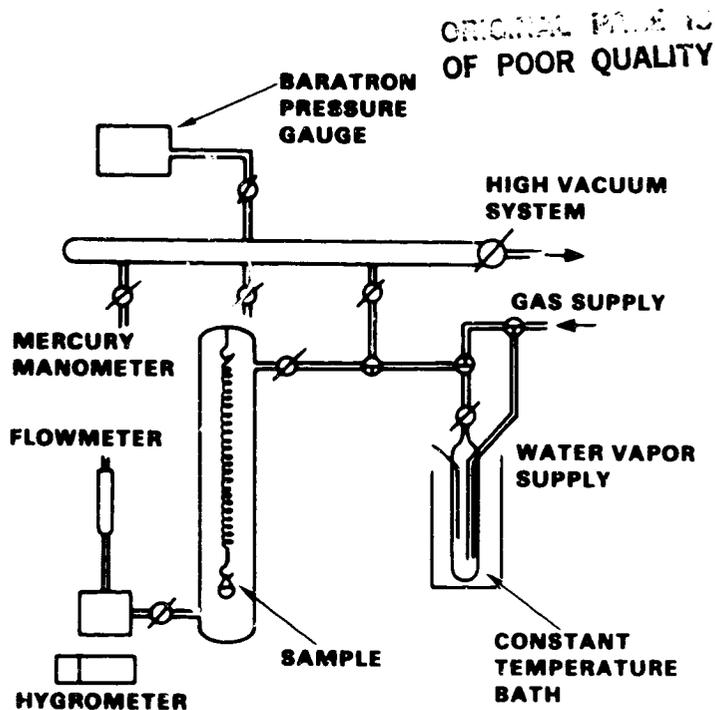
Gravimetric McBain Balance

Equilibrium CO₂ and water adsorption capacities of carbon molecular sieves were measured with a McBain quartz balance. The apparatus is illustrated in Figure 2-5. It consists of a quartz spiral spring with a cathetometer for precise measurement of the extension of the spring, a gas supply system, and a high vacuum system.

The spring is contained in a quartz tube, and carbon molecular sieves are contained in a quartz basket hung from the end of the quartz spring. Three springs were used in this study with spring constants of 0.989, 2.71, and 2.94 mg/mm at 25°C. Two baskets weighting 49.5 and 311.5mg were used throughout this program. The extension of the spring could be measured to ±0.05 mm by the use of the cathetometer.

At the start of the measurement, about 100 mg of carbon molecular sieve were evacuated and heated to 200°C for about one hour. The pressure of the system was monitored by a McLeod mercury manometer and a Baratron pressure transducer. Although one hour may not be long enough to drive off all gases





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Figure 2-5. McBain Balance Apparatus

adsorbed on the carbon molecular sieve, the capacities measured are realistic in terms of actual operation in an adsorption/desorption bed. To avoid detectable variations in the spring constant as a function of temperature, the adsorption measurement was carried out after the adsorbent and the quartz spring were cooled to room temperature under vacuum.

The adsorbate was introduced into the adsorption chamber from the gas supply system as shown in Figure 2-5. Desired vapor pressures of CO_2 were supplied by flowing CO_2 /air mixtures containing CO_2 at 0.4, 0.5, 1.0, and 5.0 percent. Water vapor pressures were generated by a water reservoir immersed in a constant temperature bath. The dew points of the static water vapor and the flowing CO_2 gas mixtures were monitored by a hygrometer at the downstream end of the adsorption column. Water saturated gases could be introduced into the McBain balance by passing the gas mixture through the water reservoir.

The CO_2 adsorption was found to be fast. It usually took about 20 minutes or less to reach an equilibrium under the experimental condition. However, water adsorption was very slow. Equilibrium conditions were not reached for hours or even days. At equilibrium, the adsorption chamber was isolated from the rest of the system. The spring extension was measured under static conditions to ensure that the gas flow did not affect the measurement.

Dynamic Adsorption/Desorption Bed

For measuring selective adsorption of CO_2 from air under dynamic conditions, a dynamic adsorption/desorption test bed was set up as shown in Figure 2-6. The principal features of the test bed include a pyrex column (1.0 cm ID x 26 cm long), a tube furnace, a gas handling system, a gas chromatographic analyzer, and a hygrometer. The column has a volume of 20 ml, and can be heated and evacuated. CO_2 /air mixtures with CO_2 concentration of 0.4, 1.0, and 5 percent were supplied from pre-mixed gas tanks. The moisture content of the gas, before and after the test column, was measured by a YSI

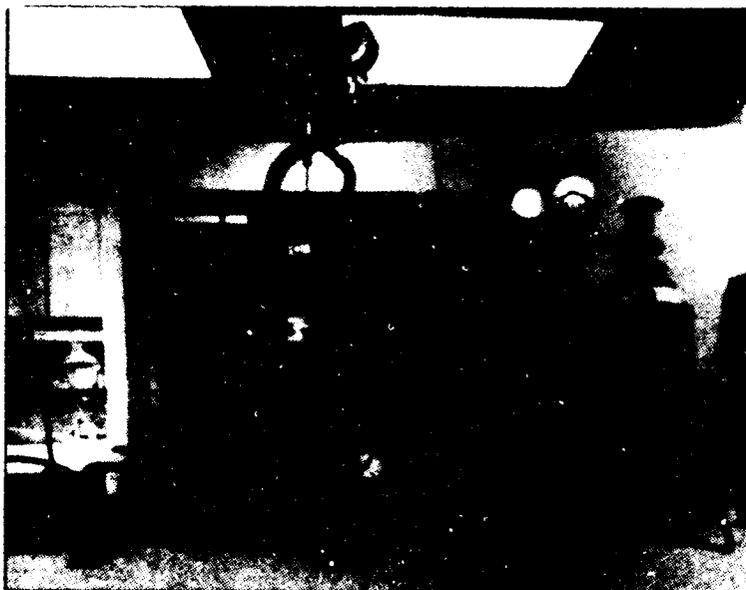


Figure 2-6. Dynamic Adsorption/Desorption Test Bed

model 91 Dew Point Hygrometer (Yellow Springs Instrument Co.). Gas compositions in the inlet and outlet streams were determined by the Hewlett-Packard 5890A gas chromatographic unit used for the screening and characterization of carbon molecular sieves.

About 15g of pelletized carbon molecular sieve bound with asphaltene and sulfite pulp liquor were packed into the adsorption column and evacuated at 200°C for several hours. CO₂/air mixture was then introduced at a flow rate of 700 ml/min, which corresponded to a gas residence time of 1.7 sec. Effluent gases coming out of the adsorption bed passed through a 0.1 mL sampling valve of the gas chromatograph. The gas chromatograph was equipped with a 2 mm ID 56 cm column which completed a single analysis of the effluent mixture in 2 min. Samples of the effluent could, therefore, be analyzed at intervals of 2 1/2 minutes. Break-through curves of CO₂ on carbon molecular sieves were determined from the effluent gas compositions.

For desorption, He carrier gas was introduced at 700 mL/min while the adsorbent was heated to a desorption temperature. The desorbed gases were analyzed by the same gas chromatograph. The desorbed gases could be collected into a fixed evacuated volume. Gas compositions could be determined for the total CO₂ desorbed, and for possible trace contaminants.

RESULTS AND DISCUSSION

Preparation of Carbon Molecular Sieves

More than 90 sorbents were prepared from 10 different polymer precursors. The starting materials identified previously were selected because they offer the best possibility of forming adsorbents for the selective removal of CO₂ from air. An additional consideration for the choice of the polymer precursor was that the precursor contain no oxygen. Any oxygen functional groups in the



precursor material will tend to form oxygen surface complexes on the carbonized product. This will result in the formation of polar sites for the adsorption of water.

Most of the carbon molecular sieves prepared in this program were carbonized in nitrogen at a flow rate of 150 ml/min. Carbonization temperature was increased at a rate of 110°C/hr to a final temperature that was maintained for 1-1/2 hr. Carbon molecular sieves prepared under these conditions are summarized in Table 2-3. Sorbents are identified by four letters and a number. The letters are a code name for the starting polymer as defined in the table. The dash number defines the preparation temperature, starting with -1 = 400°C, -2 = 500°C, etc. For example, CCSD-6 was prepared starting with the F-278 copolymer at a temperature of 900°C.

TABLE 2-3
CARBON MOLECULAR SIEVES PREPARED AT A HEATING RATE OF 110°C/HR
UNDER NITROGEN FLOW OF 150 ML/MIN

Sorbent	Starting Polymer	Final Temperature, °C
CCSA	PVDF	450, 600, 800, 950
CCSB	AN	600, 800
CCSC	AN-Modified	600
CCSD	PVDC-PVC (F-278)	600, 800, 900, 950, 1000, 1100
CCSE	PVDC-PVC (F-310)	600, 800
CCSF	PVDC-AN	600, 800, 950
CCSG	PS-DVB-CS	550, 800, 900, 1000
CCSH	PS-DVB-ES-861	550
CCSI	PS-DVB-XAD	550
CCSJ	HGR-805	900

During the evaluation of the hydrophobic property of the adsorbent, the carbon molecular sieve adsorbed more water than anticipated for this type of adsorbent. One reason for this behavior was attributed to the presence of oxygen (~0.1 percent) detected in the nitrogen used in the adsorbent synthesis. Later adsorbents were prepared in the presence of helium, which contained a small amount of oxygen (<0.02 percent). Carbon molecular sieves prepared in helium are identified in Table 2-4.

To assess the effects of heating rate and carbonization soaking time on the performance of the carbon molecular sieve, several preparations were carried out at different heat-treatment conditions. These syntheses are identified in Table 2-5.



TABLE 2-4

CARBON MOLECULAR SIEVES PREPARED AT A HEATING RATE OF 110°C/HR
UNDER HELIUM FLOW OF 150 ML/MIN

Sorbent	Starting Polymer	Final Temperature, °C
CCSA-H	PVDF	900, 1000, 1200
CCSK-H	HALAR	560, 800, 900, 1000
CCSL-H	PVDC	900, 1000

TABLE 2-5

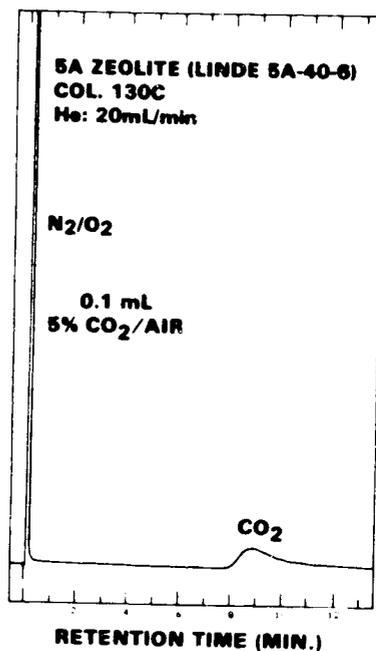
CARBON MOLECULAR SIEVES PREPARED AT A HEATING RATE
OF 150°C/HR UNDER HELIUM FLOW OF 150 ML/MIN

Sorbent	Starting Polymer	Heating Rate	Final Temperature, °C
CCSA-H150	PVDF	150	1000, 1100
CCSL-H150	PVDC	150	1000, 1100
CCSL-H300	PVDC	300	900, 1000

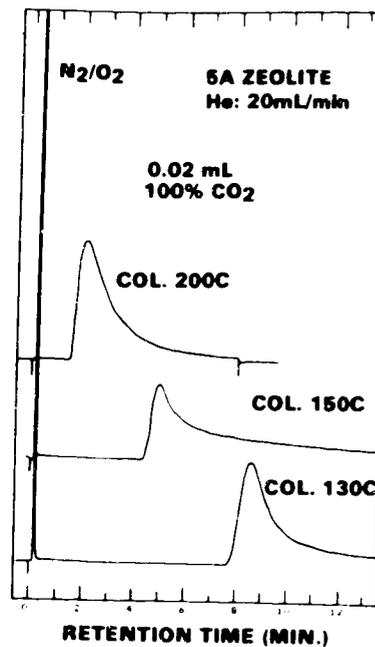
In total, 40 different carbon molecular sieves were prepared in this study program. Among these newly prepared carbon molecular sieves, 33 were found to be selective for the adsorption of CO₂ from air. Evaluation of their selectivity, hydrophobicity, and other adsorption/desorption characteristics are detailed below.

Dynamic CO₂ Adsorption on Zeolite 5A

Zeolite 5A was investigated in this program to provide baseline data for comparison. This zeolite adsorbs both CO₂ and H₂O strongly. In the absence of moisture, CO₂ is preferentially adsorbed from air as shown in Figure 2-7. At room temperature (32°C), CO₂ was adsorbed so strongly that the gas was eluted very slowly. As the temperature increases, the retention time of CO₂ decreases. However, even at temperatures as high as 130 to 200°C, CO₂ retention times remain relatively long under our chromatographic evaluation conditions (Figure 2-7b). The elution profiles of CO₂ showed heterogeneity of the adsorbent as tailings were observed in all of the chromatograms taken. This may be caused by inhomogeneity of the zeolites synthesized, or by the binder material used in the commercial zeolite adsorbent.



a.



b.

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Figure 2-7. Dynamic CO₂ Adsorption On Zeolite 5A in a Gas Chromatographic Column

The long CO₂ retention time (see Figure 2-7a) indicates effective adsorption of CO₂ from air by the 5A zeolite. However, temperature data indicates that a relatively high temperature and/or high vacuum are required for the desorption of CO₂ from the adsorbent. The latter characteristic is not desirable for the removal and recovery of CO₂ in the air revitalization system. The effects of strong binding of CO₂ and moisture on zeolite 5A for the CO₂ removal in a space station will be discussed in later sections.

Dynamic CO₂ Adsorption on Carbon Molecular Sieves

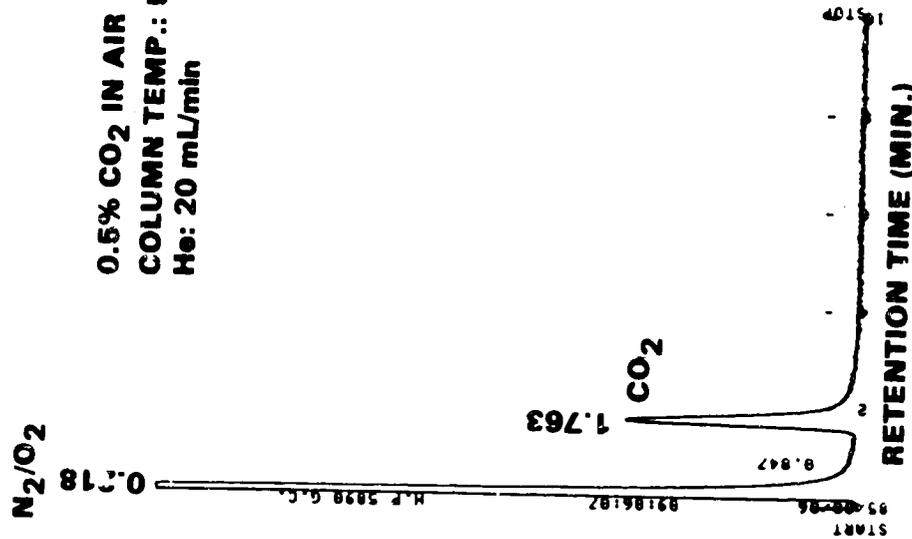
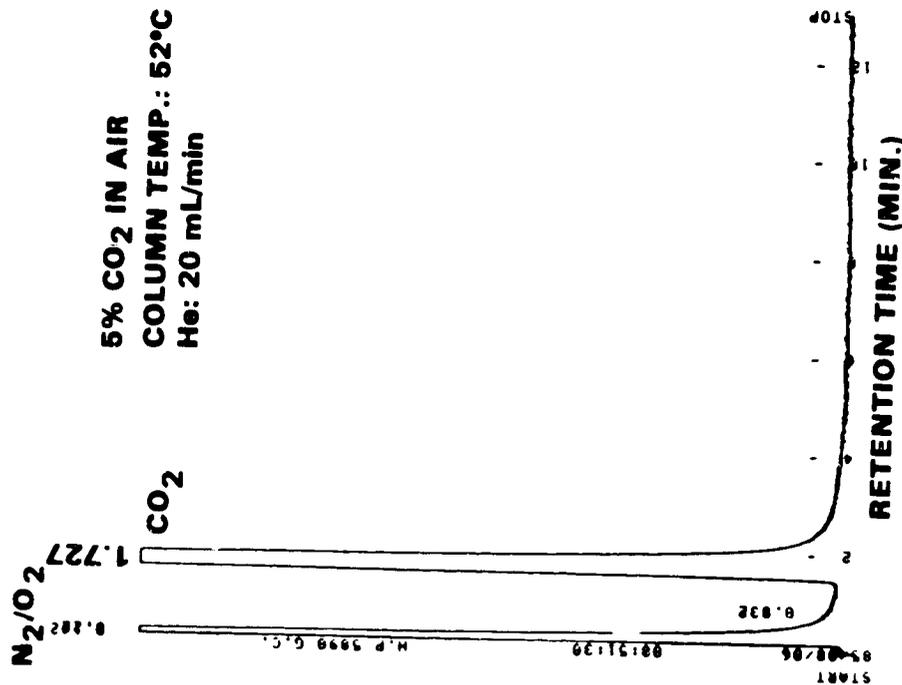
Most of the carbon molecular sieves prepared in this study showed selectivities for CO₂ over N₂/O₂. Dynamic CO₂ adsorption on the carbon molecular sieves in the GC column is illustrated in Figures 2-8, 2-9, and 2-10. Some selected gas-chromatographic data for carbon molecular sieves are presented in Tables 2-6 and 2-7. Gas-chromatographic data obtained for dealuminated zeolites and some commercial carbon molecular sieves are listed in Tables 2-8 and 2-9, respectively, for comparison.

Carbon molecular sieves exhibit shorter CO₂ retention times than 5A zeolite (Tables 2-6, 2-7, and 2-8). These CO₂ retention times decrease to low values at relatively low temperatures (e.g., 110°C) indicating that the desorption of CO₂ can be accomplished at lower temperatures on carbon molecular sieves than on 5A zeolite. This is beneficial in terms of energy consumption in the CO₂ removal in a space station. During the earlier phase of this study, a number of commercial carbon sieves were obtained and studied.





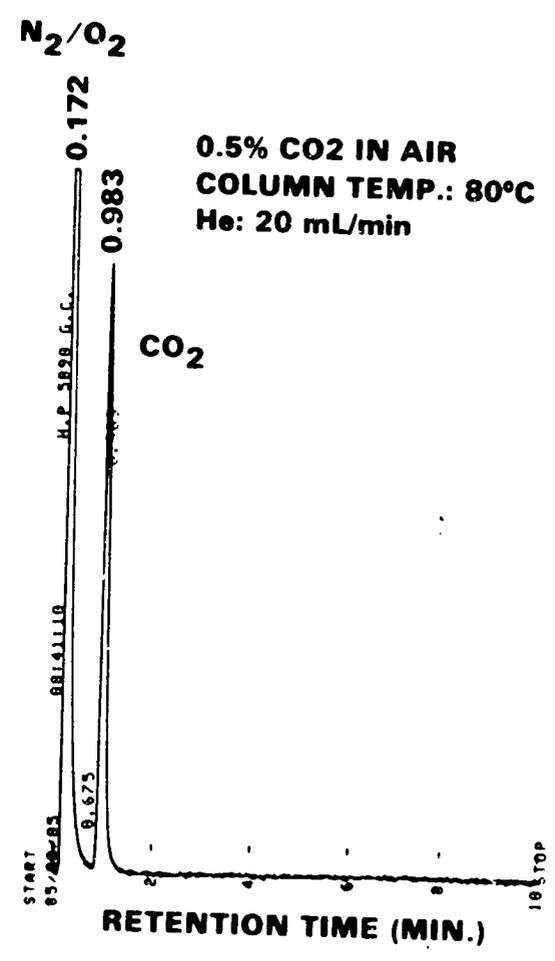
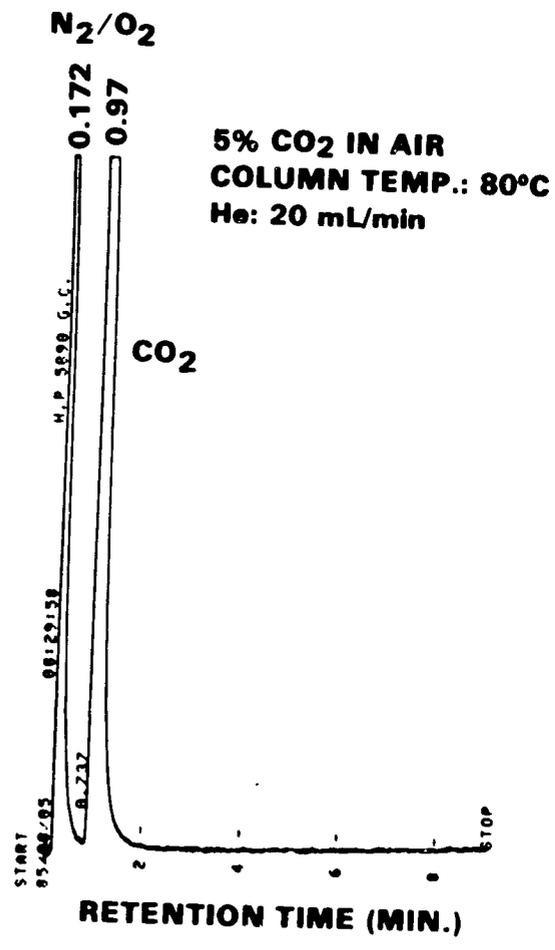
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CCSD-6 SELECTIVE FOR CO₂ AND LIGHTLY BOUND TO SORBENT

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Figure 2-8. Dynamic CO₂ Adsorption on CCSD-6 (GC Data)



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Figure 2-9. Dynamic CO₂ Adsorption on CCSC-3 (GC Data).

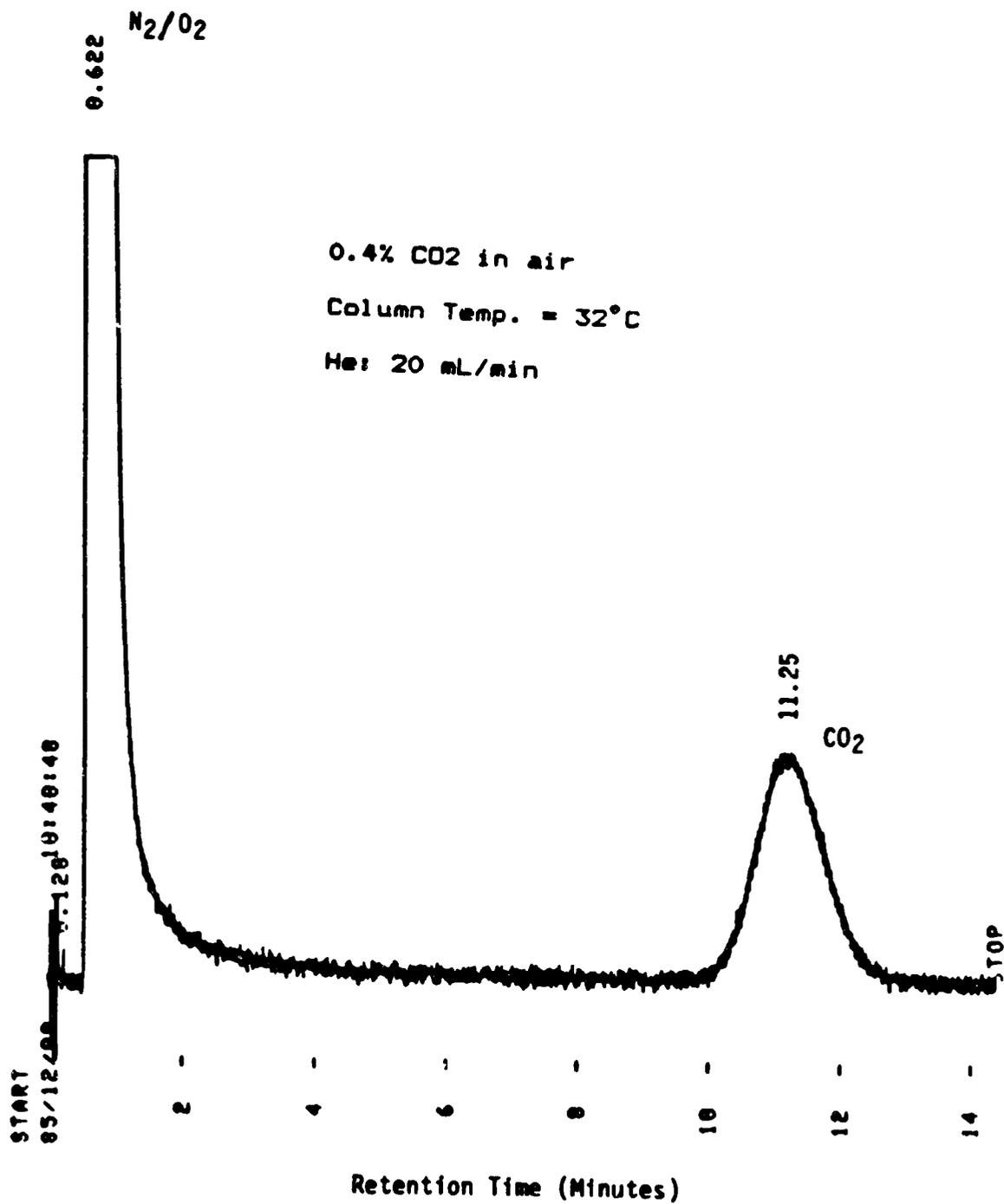


Figure 2-10. Dynamic CO₂ Adsorption on CCSL-H300-7 (GC Data).

TABLE 2-6

SELECTED GAS-CHROMATOGRAPHIC DATA FOR CARBON MOLECULAR
SIEVE PREPARED UNDER NITROGEN ATMOSPHERE

SORBENT *	PACKING DENSITY, g/ML	CO ₂ RETENTION TIME (MIN) AT		
		32°C	110°C	150°C
CCSA - 1.5	0.53	5.2	0.6	0.3
- 3	0.57	16.0	1.5	0.7
- 5	0.58	20.9	1.8	0.8
- 6.5	0.53	18.4	1.7	0.8
CCSD 3	-	2.9	0.4	
- 5	0.16	3.8	0.4	
- 6	0.15	3.5	0.5	
- 6.5	-	3.7	-	
- 7	-	**	-	
- 8	-	**	-	
CCSF - 3	-	4.3	0.5	
- 5	0.19	8.5	0.8	
- 6.5	0.25	5.9	0.3	0.3
CCSG - 2.5	-	4.0	0.6	0.3
- 5	0.49	10.4	1.0	0.5
- 6	0.55	-	1.8	1.1 (140°C)
- 7	0.54	16.3	1.7	1.0 (140°C)

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* Refer to Table 2-3 for sorbent identification.

** Not measurable indicating no separation between CO₂ and air

TABLE 2-7

SELECTED GAS-CHROMATOGRAPHIC DATA FOR CARBON MOLECULAR SIEVES
PREPARED UNDER HELIUM ATMOSPHERE

Adsorbent	Packing Density, g/ml	CO ₂ Retention Time, Min		
		32°C	110°C	140°C
CCSA-H-6	0.50	20.1	1.9	1.0
- 7	0.47	16.7	1.6	0.9
- 9	0.43	10.5	1.2	0.7
CCSK-H-2.5	0.53	18.6	1.7	0.9
- 5	0.48	19.1	1.7	0.9
- 6	0.43	16.0	1.5	0.9
- 7	0.47	17.9	1.7	1.0
CCSL-H-6	0.21	9.0	1.0	0.6
- 7	0.20	8.7	1.0	0.4
CCSA-H150-7	0.51	22.3	1.9	1.0
- 8	0.49	17.1	1.7	1.0
CCSL-H150-7	0.26	11.4	1.2	0.7
- 8	0.30	10.2	1.2	0.7



TABLE 2-8

GAS-CHROMATOGRAPHIC DATA FOR DEALUMINATED ZEOLITES
OBTAINED FROM COMMERCIAL SOURCES

ADSORBENT	Si/Al	PACKING DENSITY (g/ML)	CO ₂ RETENTION TIME (MIN) AT			
			32°C	110°C	150°C	200°C
5A ZEOLITE	1	0.74	>26	15.0	5.0	2.2
USY-6	7	0.69	4.2	0.7	0.4	-
USY-10	63	0.47	0.8	0.2	-	-
SILICALITE-1	∞	0.71	-	1.2	0.9 (140°C)	0.4
CCSD-6	-	0.15	3.5	0.5	-	-

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TABLE 2-9

GAS-CHROMATOGRAPHIC DATA FOR CARBON MOLECULAR SIEVES
OBTAINED FROM COMMERCIAL SOURCES

Adsorbent	Packing Density, g/ml	CO ₂ Retention, Min		
		32°C	110°C	140°C
HGR-805	0.52	9.8	1.0	0.5 (150°C)
Carbosphere	0.53	7.8	1.0	0.6 (150°C)
Carbosieve S-II	0.63	18.2	1.9	1.1
Carbosieve G	0.28	7.0	0.9	0.5



These carbon sieves selectively adsorb CO₂ and they appear to be more hydrophilic than some of the carbon sieves prepared in this study. However, the commercial carbon sieves are low in CO₂ capacity at low CO₂ pressures. Hydrophobicity and CO₂ capacity will be discussed later.

Literature shows that the hydrophilic characteristic of the inorganic zeolite is due to the polar nature of aluminum-oxygen tetrahedron (AlO₄) existing in this type of adsorbent. Replacement of the aluminum-oxygen tetrahedron with silicon-oxygen tetrahedron will decrease the polar nature of the zeolite, thus decreasing the hydrophilicity of the material. Two de-aluminated Y-faujasites and a microporous crystalline silica, Silicalite-1, were investigated to see if these "hydrophobic" zeolites would have sufficient CO₂ capacity. Gas-chromatographic screening data (Table 2-8) show that these adsorbents are selective for CO₂ over N₂/O₂. The CO₂ retention time appears to decrease as the Si/Al ratio increases for the Y-faujasite. However, both the de-aluminated Y-faujasite and Silicalite-1 suffer from a relatively low CO₂ capacity and relatively high hydrophilicity compared with some carbon molecular sieves prepared in this investigation.

Hydrophobicity of Carbon Molecular Sieves

The relative hydrophobicity of the carbon molecular sieve was investigated in the gas-chromatographic system by injecting 0.02 microliter of liquid water and measuring the retention time of water. In order to avoid condensation of water in the GC system, the adsorbent column was heated to greater than 110°C. Water retention times of some selected carbon molecular sieves and zeolite adsorbents are summarized in Tables 2-10 and 2-11.

Zeolitic materials investigated in this study all exhibited strong adsorptions of water. Although the ratio between silicon tetrahedron and aluminum tetrahedron had been greatly increased to minimize the polar nature of the adsorbent, long water retention times were measured. The adsorption of water can be attributed to the zeolite crystal and/or the binder material. Typical binders used in the commercial zeolites are clays that adsorb water. The Silicalite-1 adsorbent was bound with pure silica heat-treated to 1000°C. However, results obtained in this study indicate that this binder is not adequate for achieving a hydrophobic adsorbent.

Carbon molecular sieves are more hydrophobic than zeolites, especially carbosphere and some carbon adsorbents prepared in this study. Competitive adsorptions between CO₂ and water were evaluated by a cyclic coadsorption and "pre-wetting" of the adsorbent in the GC column. At a column temperature of 52°C, repetitive chromatograms were obtained by injecting 0.4 percent CO₂/air mixture saturated with water at 22°C. As shown in Table 2-12, the difference between CO₂ and air (N₂/O₂) remains constant for 30 cycles indicating that water in CO₂ gas mixture does not significantly affect the selective adsorption of CO₂ over N₂ and O₂.

The CO₂ adsorption was further studied on a water-saturated GC column. The adsorbent column was saturated with water by passing the gas through a water bath at about 20°C. To maintain a constant water vapor pressure, the CO₂ test gas was also saturated with water at the same temperature (see Table 2-13).



TABLE 2-10

WATER RETENTION TIMES FOR SOME SELECTED CARBON
MOLECULAR SIEVES AND ZEOLITE ADSORBENTS

SORBENT	COLUMN TEMPERATURE, °C	RELATIVE RETENTION TIME (MIN)	
		N ₂ /O ₂	H ₂ O (NoCO ₂)
5A ZEOLITE	220	0.21	*
USY-10	140	0.15	~ 28
SILICALITE - 1	200	0.14	~ 30
CCSD - 4.5	140	0.17	0.96
CCSD - 6	140	0.14	2.00
CCSG - 5	140	0.16	0.79
CCSG - 6	140	0.29	0.91
CCSG - 7	140	0.23	0.72

*NOT OBSERVED INDICATING VERY STRONG H₂O ADSORPTION

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TABLE 2-11

WATER RETENTION TIMES FOR CARBON MOLECULAR SIEVES OBTAINED
FROM COMMERCIAL SOURCES

Adsorbent	Column Temperature, °C	Retention Time, Min	
		N ₂ /O ₂	H ₂ O (NoCO ₂)
HGR-805	140	0.17	4.28
Carbosphere	160	0.29	1.47
Carbosieve S-11	140	0.27	4.00
Carbosieve G	110	0.24	1.89



TABLE 2-12
CYCLIC COADSORPTION BEHAVIOR OF CCSG-7

COLUMN TEMPERATURE: 52°C
0.4% CO₂ SATURATED WITH H₂O AT 22°C
DRY He CARRIER GAS AT 20 ML/MIN

NUMBER OF INJECTION CYCLES	RETENTION TIME, MIN		
	N ₂ /O ₂	CO ₂	Δ
0 (DRY 0.4% CO ₂)	0.56	8.30	7.73
1	0.60	8.30	7.70
2	0.60	8.30	7.70
5	0.60	8.30	7.70
10	0.59	8.30	7.71
15	0.60	8.30	7.70
20	0.59	8.30	7.71
25	0.60	8.30	7.70
30	0.60	8.28	7.68

REPEATED INJECTIONS OF 0.4% CO₂ SATURATED WITH H₂O SHOW NO CHANGE IN CO₂ RETENTION TIME

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TABLE 2-13

CO₂ ADSORPTION ON
H₂O SATURATED GC COLUMN

● EXPERIMENTAL PROCEDURE

1. SORBENT COLUMN SATURATED BY CARRIER GAS AT 100% RH AND ABOUT 20°C
2. INJECTION OF 0.4% CO₂ AIR SATURATED WITH H₂O AT ABOUT 20°C

● TEST RESULTS

- GOOD SEPARATION BETWEEN CO₂ AND N₂/O₂ WITH ONLY SMALL LOSS IN CO₂ RETENTION TIME

● CONCLUSION

- TEST DATA DEMONSTRATE CARBON SORBENT CO₂ SELECTIVITY OVER H₂O

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For zeolite 5A, the column was maintained at 110°C. As shown in Figure 2-11, the column exhibited a CO₂ retention time of 18.1 minutes for 0.4 percent CO₂ with dry adsorbent. However, the adsorbent lost almost all of its capacity for CO₂ after the adsorbent had been saturated with water at 2.9 percent relative humidity. These results indicate the strong preference of the zeolite adsorbent for water over CO₂; they are consistent with results of long water retention time even at 220°C (see Table 2-10).

For carbon molecular sieves, the effects of moisture on the CO₂ adsorption are illustrated in Figures 2-12 to 2-14. As shown in these figures, good separation between CO₂ and N₂/O₂ were observed when the carbon molecular sieves were saturated with water at high relative humidities (83.8 percent). However, some loss in the CO₂ retention time was measured. This suggests that some adsorption sites have been occupied by water under the experimental conditions. The extent of the loss in CO₂ retention time appears to depend on the precursor material and the carbonization conditions.

Although all precursors chosen for this study were derived from monomers containing no oxygen functional groups, it is well known that most common initiators used in the commercial production of polymers contain oxygenated species. The amount used in the polymerization is typically on the order of 0.1 percent. However, during the carbonization for the synthesis of carbon molecular sieves, the oxygenated initiator may oxidize the surfaces of the pores in these adsorbents. This would result in some adsorption sites that are selective for water due to the oxygenated surface groups.

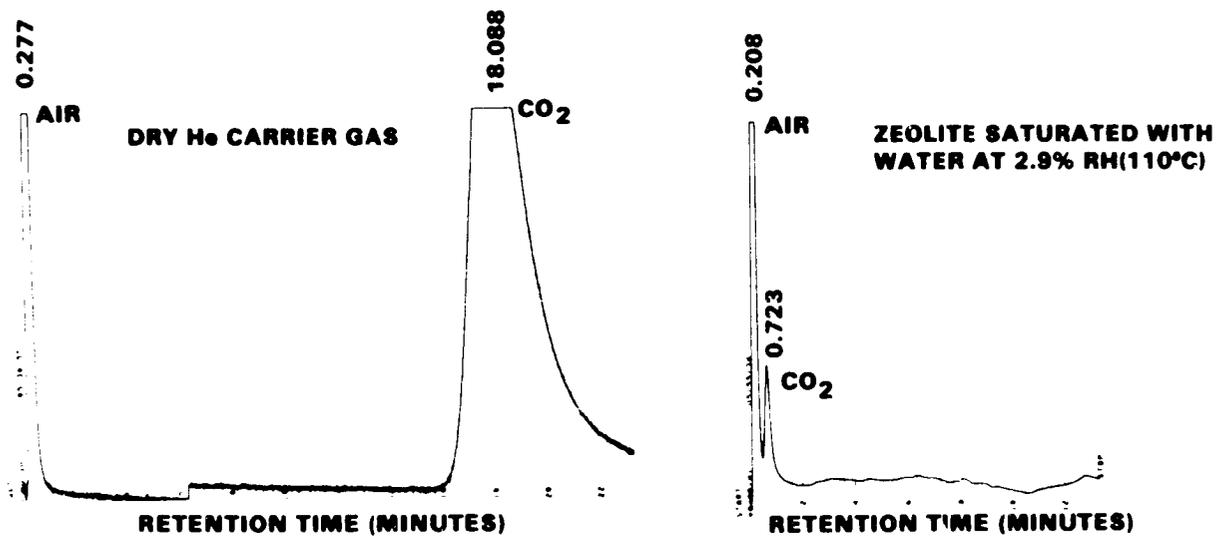
In addition to the oxygen-containing initiator, any trace amount of oxygen in the nitrogen or helium gas used in the preparation of carbon molecular sieves will also affect the property of the adsorbent. During the earlier part of our synthesis study, laboratory nitrogen was used as an inert gas in the contained about 0.1 percent oxygen. The use of a pure helium with an oxygen content of 0.02 percent decreased the relative retention of H₂O (see Table 2-14). This also minimizes the decrease in CO₂ retention time in the CO₂ adsorption study on the water saturated GC column (see Figure 2-14). For the synthesis of hydrophobic carbon molecular sieves, care should be taken to avoid any contamination with oxygenated species in the synthesis mixture to minimize the formation of any hydrophilic sites.

Equilibrium CO₂ Adsorption Capacity

Carbon molecular sieves that showed promise as effective adsorbents for the CO₂ removal as a result of the GC screening tests were further investigated to determine CO₂ capacity. Equilibrium CO₂ adsorption capacity of a number of adsorbents were measured on the McBain balance at CO₂ partial pressures of 0.5, 1.0, and 5.0 kPa. Results of the measurement on zeolite 5A and carbon molecular sieves prepared from 4 different polymer precursors are presented in Table 2-15. These capacity values are compared with those of commercial carbon molecular sieves as shown in Table 2-16. At 25°C, dry zeolite 5A exhibits high capacities for CO₂ capacity decreases drastically with a small amount of water adsorbed on the zeolite. According to Dell'Osso and Winnick, the CO₂ capacity decreased from 0.040 to 0.007 g/g-adsorbent at a CO₂ partial

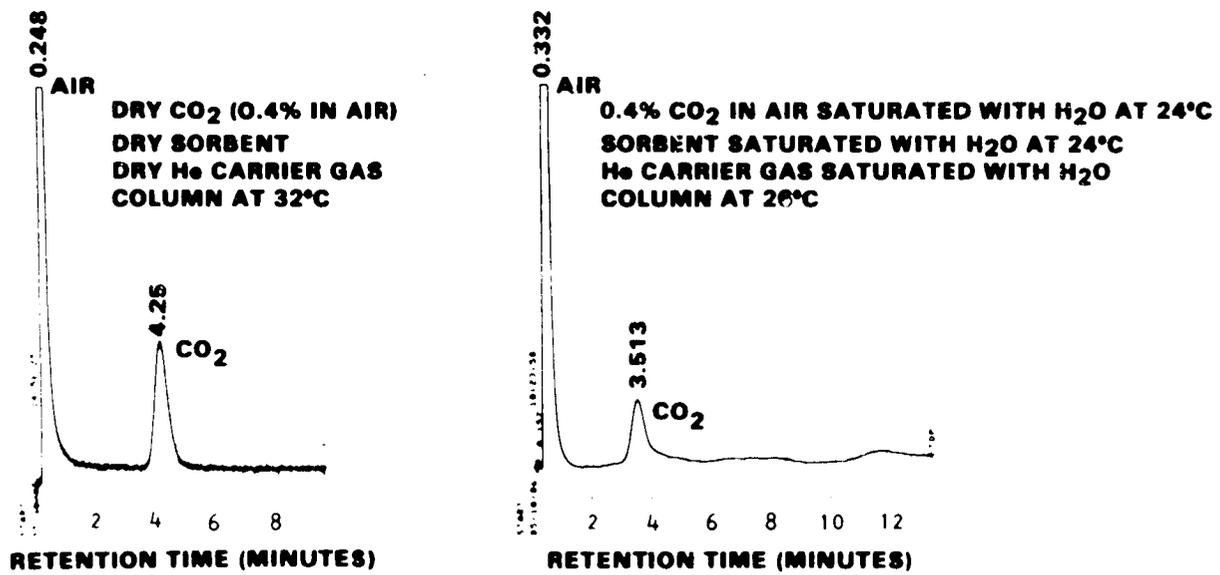


**COLUMN TEMPERATURE: 110°C
0.4% CO₂ SATURATED WITH H₂O AT 24°C**



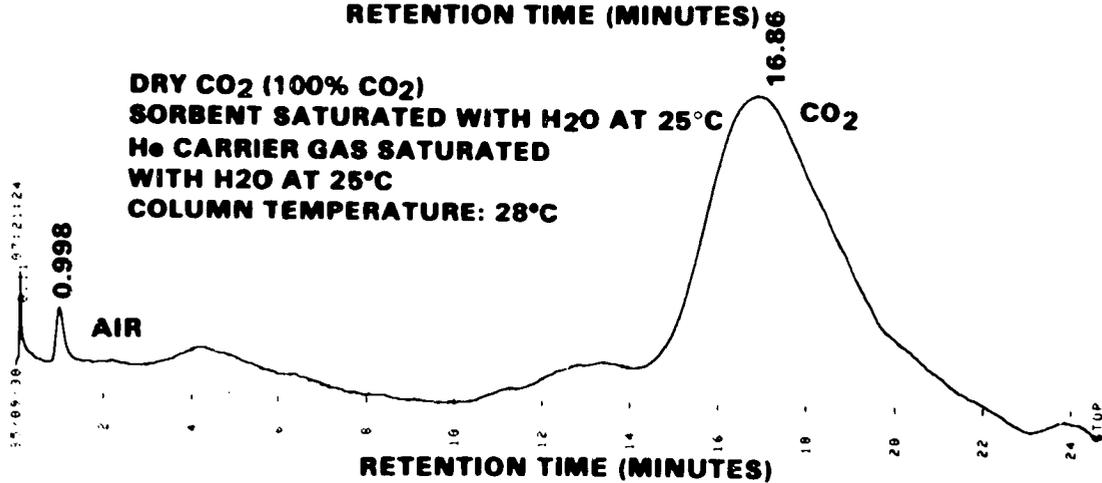
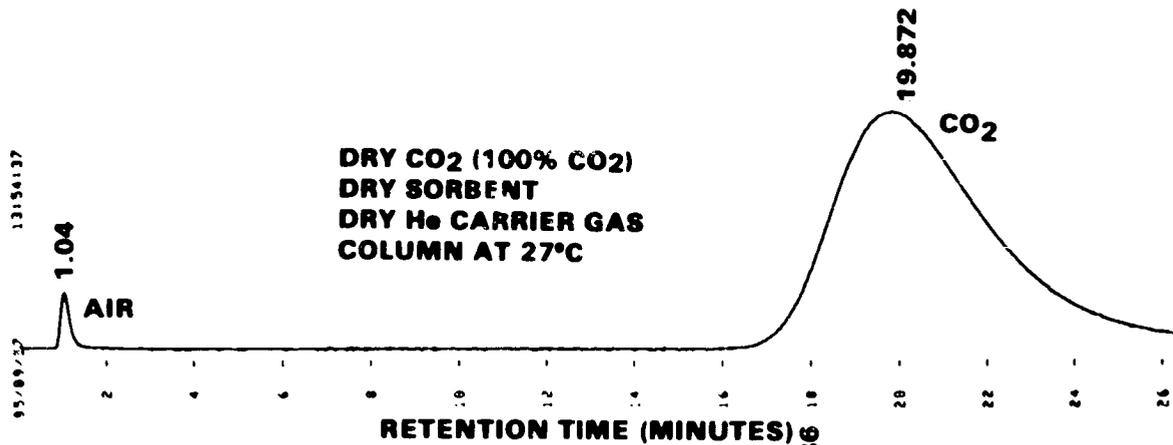
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Figure 2-11. CO₂ Retention Time on Dry and Wet Zeolite 5A



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Figure 2-12. CO₂ Retention Time on Dry and Wet CCSD-6



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Figure 2-13. CO₂ Retention Time on Dry and Wet CCSG-6



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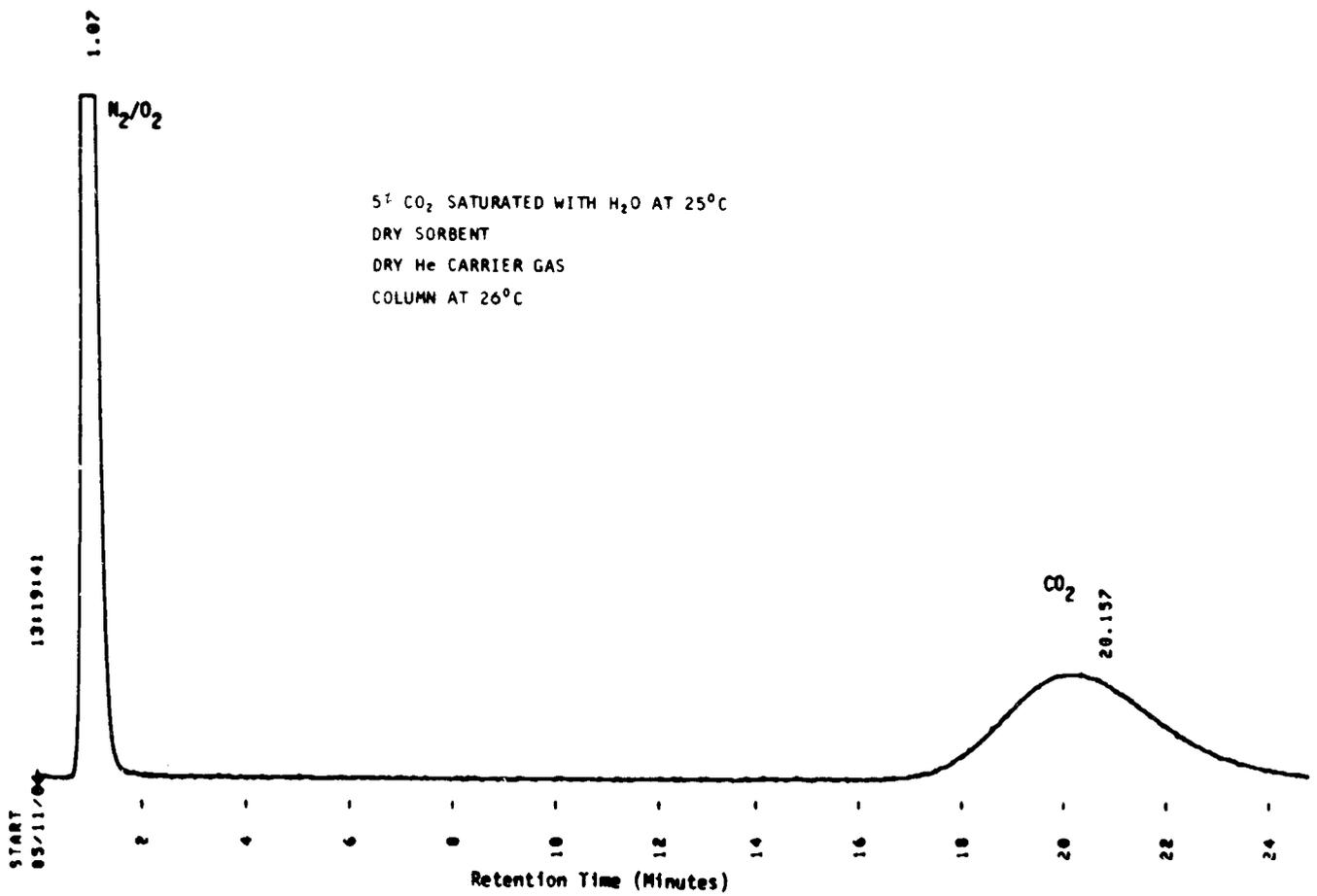


Figure 2-14a. CO_2 Retention Time on Dry and Wet CCSA-H-7 at $26^\circ C$



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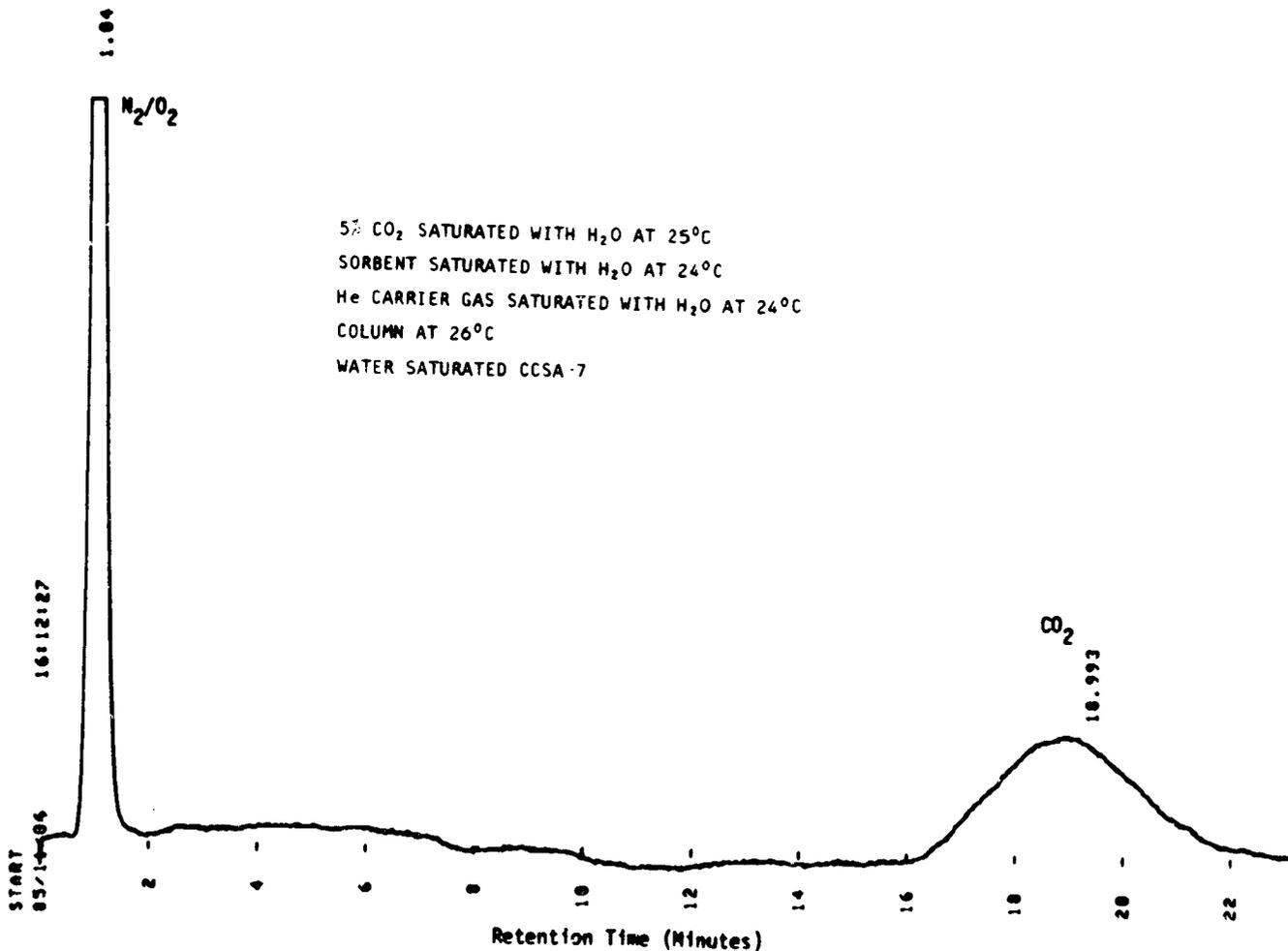
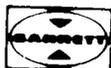


Figure 2-14b. CO₂ Retention Time on Dry and Wet CCSA-H-7 at 26°C



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TABLE 2-14
EFFECT OF INERT GAS ON THE HYDROPHOBICITY OF
CARBON MOLECULAR SIEVES

Adsorbent	Inert Gas Used	Packing Density, g/ml	GC Retention Times, min at 140°C		
			N ₂ /O ₂	CO ₂	H ₂ O
CCSA-6.5	N ₂	0.53	0.25	0.80	0.92
CCSA-H-6	He	0.50	0.27	1.05	0.69
CCSA-H-7	He	0.47	0.28	0.94	0.48

TABLE 2-15
EQUILIBRIUM CO₂ ADSORPTION CAPACITIES AT 25°C

SORBENT	g/g-ADSORBENT		
	0.5 kPa	1.0 kPa	5.0 kPa
CCSA - 1.5	-	0.008	-
- 3	0.017	-	0.026
- 5	-	0.021	-
- 6.5	-	0.022	-
CCSD - 3	0.015	-	0.027
- 5	0.026	0.021	0.040
- 6	0.033	0.031	0.061
- 6.5	0.020	-	0.035
- 8	0.025	-	0.035
CCSF - 5	0.018	-	0.034
- 6.5	0.021	0.024	0.037
CCSG - 5	0.018	-	-
ZEOLITE 5A DRY	0.040	0.067	-
ZEOLITE 5A WET	0.007	-	-

CCSD-6 SELECTED FOR FURTHER EVALUATION

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TABLE 2-16

EQUILIBRIUM CO₂ ADSORPTION CAPACITIES OF COMMERCIAL
CARBON MOLECULAR SIEVES AT 25°C

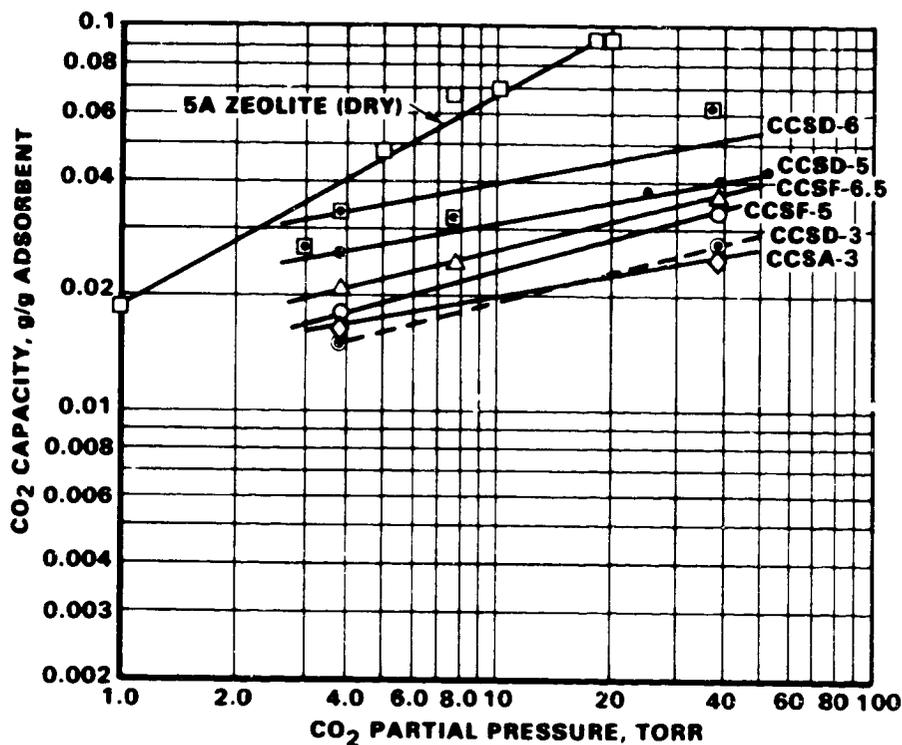
Adsorbent	CO ₂ Capacity, G/G-Adsorbent	
	0.5 kPa	5.0 kPa
HGR-805	0.014	-
Carbosphere	0.011	-
Carbosieve S-II	0.015	0.027

pressure of 0.5 kPa when water of 0.0076 gH₂O/g-adsorbent was added to the adsorbent. This is consistent with the result obtained in the present GC study, which showed that the adsorbent lost almost all of its CO₂ capacity at a relative humidity of 2.9 percent (Figure 2-11).

In the GC evaluation, commercial carbon molecular sieves showed promise as potential candidates for the selective removal of CO₂ from air. However, their CO₂ capacities (Table 2-16) and hydrophilicity (Table 2-11) proved to be inadequate for further consideration.

CO₂ adsorption isotherms of a selected number of carbon molecular sieves are illustrated in Figure 2-15 for comparison with dry 5A zeolite. Although, the isotherm data scatter somewhat, the CO₂ capacity appears to increase linearly as the CO₂ vapor pressure increases in the range of the present study. The steeper slope of the zeolite 5A indicates a higher binding energy between CO₂ and zeolite than that between CO₂ and the carbon molecular sieve. This is consistent with the gas-solid chromatographic data, which show that a higher temperature is needed for CO₂ to be desorbed from zeolite than from most of the carbon molecular sieves.

Among the carbon molecular sieves prepared in this study, the adsorbent prepared from PVDC-PVC (Saran) copolymer, CCSD-6, exhibits the highest CO₂ capacity. However, the synthesis of carbon molecular sieve from this copolymer is very sensitive to the preparation conditions. The preparation of carbon molecular sieve from this copolymer was, therefore, extensively investigated. Results of the study indicated further that formulation and physical properties of the copolymer greatly affect the adsorption characteristics of the carbon sieve. Consequently, a precursor synthesis effort was initiated to define the properties of the polymer needed to produce carbon sieves with high CO₂ capacities and hydrophobic characteristics.



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Figure 2-15. CO₂ Adsorption Isotherms

Optimization of CO₂ Capacity through Precursor Synthesis

Polyvinylidene chloride homopolymer (PVDC) was made initially since vinylidene chloride is the major component in the formulation of Saran copolymers. A non-oxygen containing initiator, 2,2'-azobisisobutyronitrile was employed to synthesize the PVDC precursor at 50 to 70°C. Carbon molecular sieves prepared from this precursor were found to be selective for CO₂. Adsorption capacities of several carbon adsorbents prepared from PVDC are summarized in Table 2-17 along with hydrophobicity data obtained from gas-solid chromatographic measurements. Results from the preliminary precursor synthesis efforts show that carbon adsorbents with relatively high CO₂ capacities can be prepared with a broader temperature range for carbonization. A higher selectivity for CO₂ over H₂O can be achieved with non-oxygen containing initiators. It is believed that the CO₂ capacity can be further improved by optimizing the molecular weight and morphology of the PVDC polymer.

In order to define the optimum properties of the PVDC-PVC copolymer for the preparation of carbon molecular sieve, vinyl chloride should be incorporated into the PVDC material by carefully controlling the uniformity and precise monomer ratio in addition to the crystallinity and molecular weight of the copolymer. This polymer optimization effort will be beneficial in achieving a most effective adsorbent for the removal of CO₂ from space station atmosphere.



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TABLE 2-17

CO₂ CAPACITY (25°C) AND HYDROPHOBICITY OF CARBON
MOLECULAR SIEVES PREPARED FROM PVDC

Adsorbent Prepared at		CO ₂ Capacity at		Retention Time, Min at 140°C		
Heating Rate, °C/hr	Final T, °C	0.5 kPa	5.0 kPa	N ₂ /O ₂	CO ₂	H ₂ O
110	900	0.022	0.040	-	-	-
150	1000	0.024	0.041	0.23	0.71	0.50
300	1000	0.024	0.042	0.23	0.75	0.56
150	1100	0.021	0.037	0.25	0.75	0.37

Temperature Effect on CO₂ Capacity

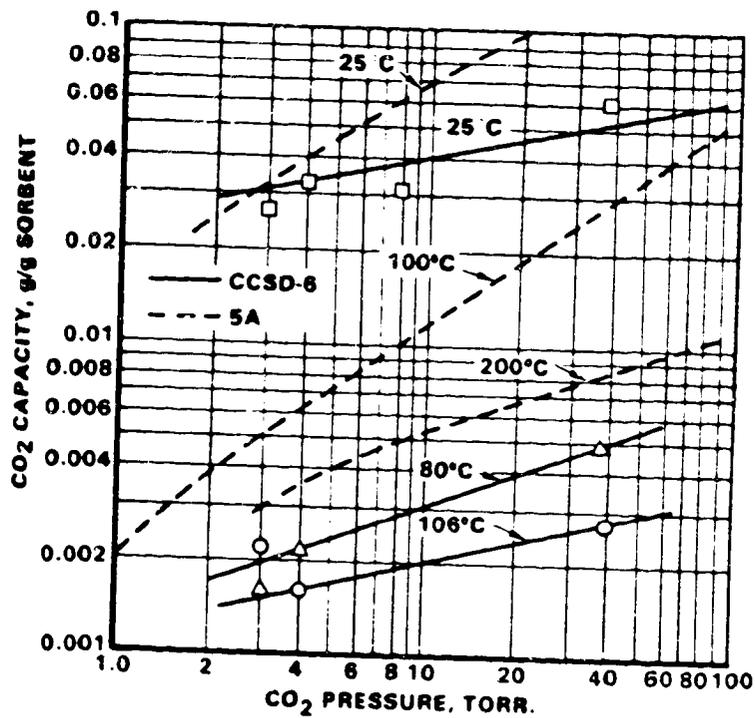
The effect of temperature on the CO₂ capacity is an important factor in the design of an adsorbent for the separation and recovery of CO₂ from air. High temperature isotherms of CO₂ on CCSD-6 adsorbent were measured at 80 and 106°C. As shown in Figure 2-16, temperature has a stronger effect on the CO₂ isotherm for carbon molecular sieve than for zeolite 5A. At a CO₂ partial pressure of about 4 mmHg (TORR), the CO₂ capacity of 5A zeolite decreases from 0.04 to 0.003g/g-adsorbent at 200°C, while the CO₂ capacity of the carbon molecular sieve decreases to 0.00065g/g-adsorbent at a temperature of 106°C. These data confirm results from a gas-solid chromatographic study that show a lower temperature is required for carbon molecular sieve than for 5A zeolite to desorb CO₂.

Equilibrium Water Adsorption on Carbon Molecular Sieves

As mentioned in the experimental section, the adsorption of moisture on the carbon molecular sieve was measured in the McBain balance. Vapor pressures of water were controlled by equilibrating water vapor with liquid water at constant temperatures. Although GC experiments have shown that carbon molecular sieves absorb CO₂ preferentially over H₂O under dynamic coadsorption conditions, these sorbents adsorb water in the McBain balance maintained at a constant water vapor pressure. The kinetics of water adsorption is very slow. It usually took several hours to several days to complete the measurement of a single point of the water isotherm.

Figure 2-17 illustrates the adsorption of water on two carbon molecular sieves, CCSA-H-7R and CCSD-6R, at 64.7 and 58.8 percent relative humidity, respectively. Water adsorption isotherms on three selected carbon molecular sieves are illustrated in Figure 2-18. At room temperatures, these molecular sieve carbons exhibit small water capacity at relative humidities lower than 40 percent. As the moisture content increases, water capacity increases.





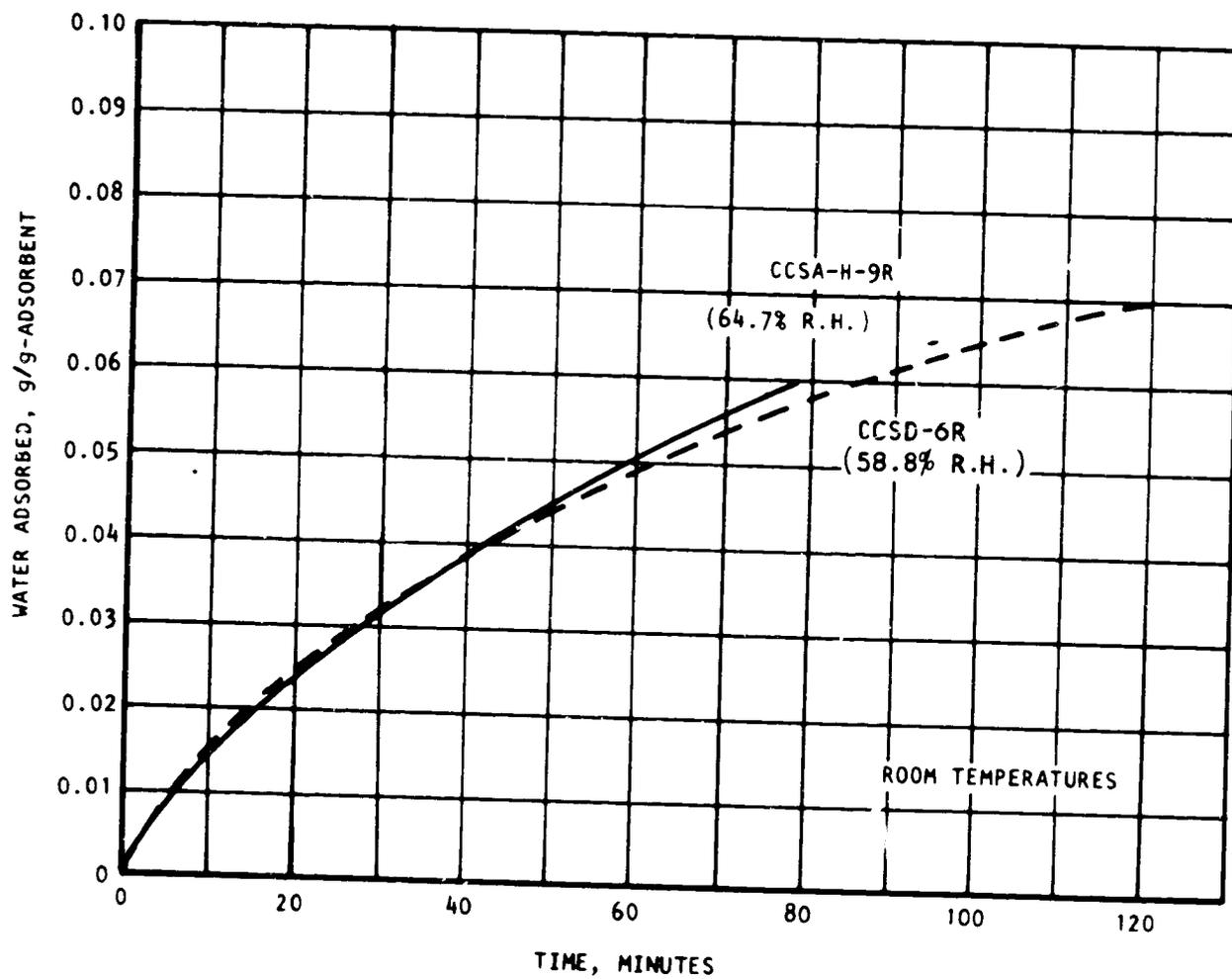
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Figure 2-16. CCSD-6 CO₂ Isotherms



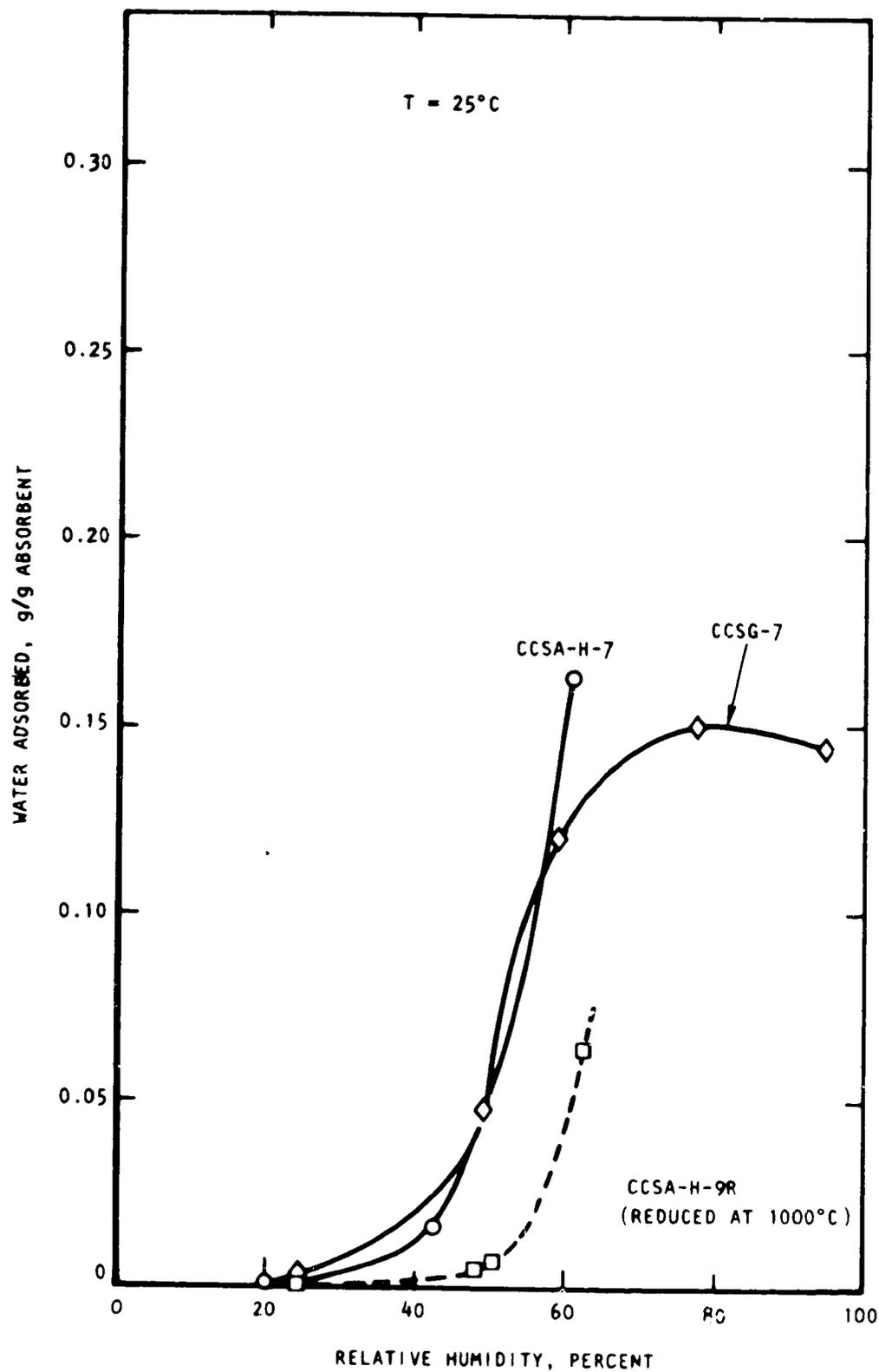
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Figure 2-17. Kinetics of Water Adsorption on Carbon Molecular Sieves



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Figure 2-18. Water Adsorption Isotherms on Carbon Molecular Sieves



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However, the extent of water adsorption is far less than that observed on zeolite 5A (see Figure 2-19).

Hydrophobicity is a relative measure of the capacity of the adsorbent for water. Isotherms of some hydrophobic porous sorbents are shown in Figure 2-19. Water adsorption on these adsorbents is generally attributed to edge sites and oxygenated surface complexes. Hydrogen reduction of the carbon sorbents significantly reduced the water adsorption by moving the isotherm to higher relative humidities (see isotherms of CCSA-H-7 and CCSA-H-9R, Figure 2-18). This indicates that some "hydrophilic" sites remained on the carbon molecular sieve even with the synthesis being carried out in helium. The reduction of the water adsorption by hydrogen treatment strongly suggests that these "hydrophilic" sites are associated with oxygenated surface species. It is believed that a detailed surface characterization will shed some light on the nature of the "hydrophilic" site. It will also permit design preparation procedures and/or surface treatment conditions for the elimination of these undesirable sites.

Trace Contaminant Analyses

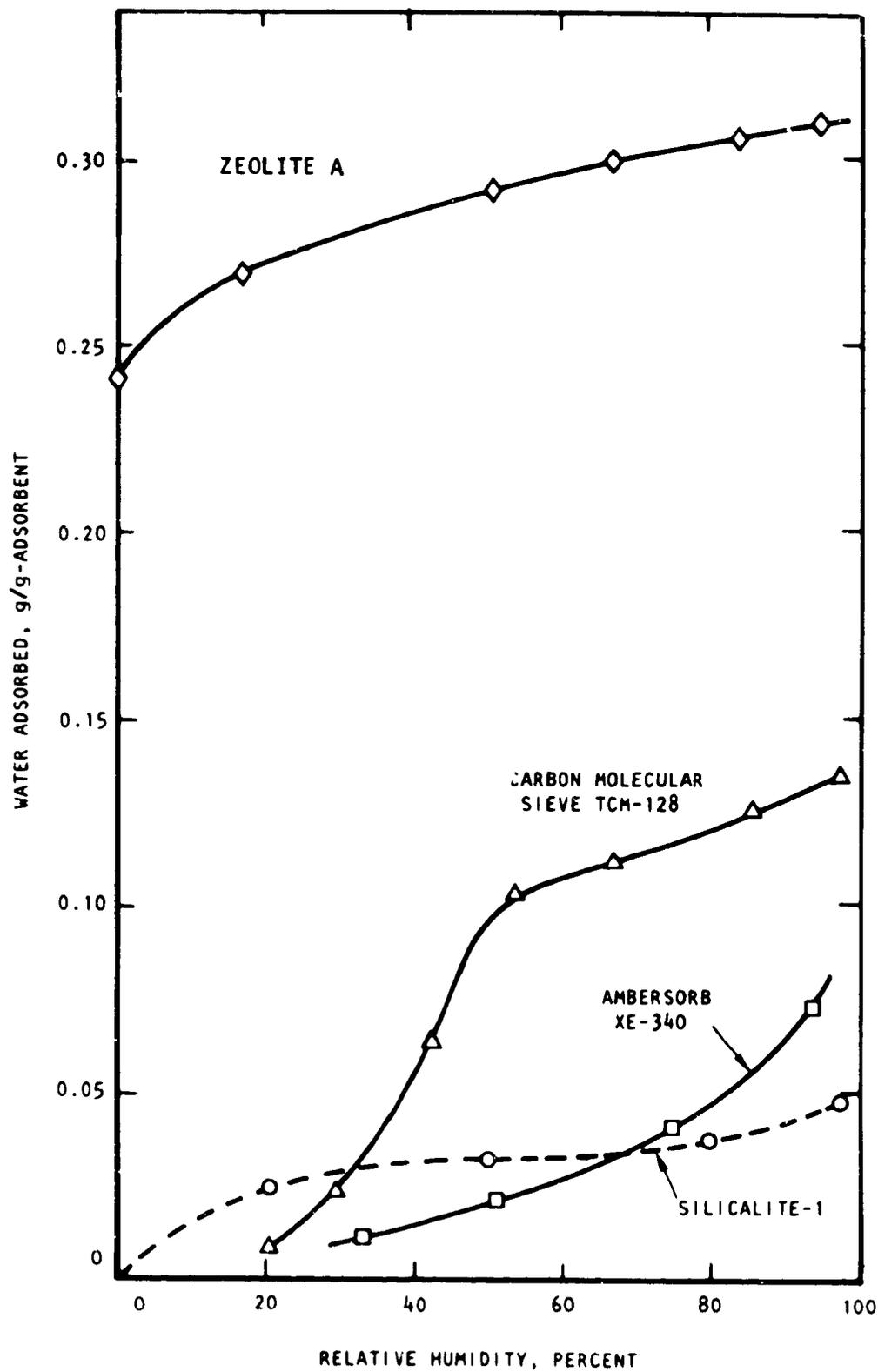
For the carbon molecular sieve to be viable as part of an air revitalization system, no trace contaminants should be generated during the adsorption/desorption of CO₂. Experiments were conducted to investigate trace contaminants that might be produced during CO₂ desorption at high temperatures. These experiments were carried out at 200°C, although GC and isotherm results had showed that CO₂ could be effectively desorbed from carbon molecular sieves at temperatures lower than 110°C.

To increase the sensitivity of the trace analysis, the bound carbon molecular sieve (CCSD-6) was heated to 200°C in the dynamic break-through test unit with a flowing gas containing 0.4 percent of CO₂ in air. Both inlet and outlet gases were collected for total and trace analyses. Results of the analysis are tabulated in Table 2-18.

TABLE 2-18
SORBENT OUTGASING TEST DATA
CCSD-6 SORBENT BED AT 200°C
TOTAL GAS ANALYSIS

Gas Component	Inlet Gas Sample		Outlet Gas Sample	
	MOL %	Mass %	MOL %	Mass %
O ₂ and/or Argon	20.8	23.0	20.7	22.9
Nitrogen	78.8	76.4	78.8	76.4
Carbon Dioxide	0.4	0.6	0.5	0.7
Total	100.0	100.0	100.0	100.0





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Figure 2-19. Water Adsorption Isotherms



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Results of the total gas analysis show that the gas composition in the outlet stream is essentially the same as that in the inlet stream. The slight increase in the CO₂ content is within the experimental uncertainty with the total gas analysis apparatus (~0.1 percent). Trace gas analysis showed no CO in the outlet stream. The following hydrocarbons were found to be less than 10 ppm, which was the detection limit of the GC analytical system.

Methane
Ethane + Ethylene
Propane
Propylene
Isobutane
N-Butane
Butene-1 + Isobutylene
Trans-2-Butene
CIS-2-Butene
Isopentane
N-Pentane
Heavies

These results show that a desorption temperature of 200°C, no detectable trace contaminants are observed. They also confirm results of earlier GC and McBain isotherm measurements that the adsorption of CO₂ is minimal on the carbon molecular sieve at temperatures higher than 110°C.

Although no detectable trace contaminants are observed in the gas collected from the dynamic break-through bed with a flowing inlet gas, any possible trace contaminants evolved from the carbon adsorbent by heating may either be diluted by the flowing gas and/or by condensation on the low temperature surfaces before they are collected. To ensure that no potentially harmful gases are evolved from the carbon adsorbent, the bound carbon molecular sieve was heated to 200°C under vacuum (10^{-4} Torr) on the solid probe of a mass spectrometer. All chemical species evolved at 100° and 200°C were ionized and detected by the mass spectrometer. Results of the mass spectrometric analysis showed trace amounts of CO, CO₂ and CH₂Cl₂. The quantities of these molecular species are very small. They are only slightly detectable above the background levels of these molecular ions in the mass spectrometer. It is reasonable to detect the evolution of CO₂ since the carbon molecular sieve was designed to adsorb CO₂ selectively. After the adsorbent had been evacuated in the mass spectrometer, some CO₂ remained to be adsorbed. This CO₂ was desorbed during the heating of the carbon adsorbent, and produced CO₂ and CO peaks because of the high energy (70 eV) electron impact ionization of the molecular CO₂.



Analysis of the CO and CO₂ peaks showed that the CO peak was higher than the normal cracking pattern of CO₂, suggesting an additional source of CO. However, the GC trace analysis indicated no CO in the outlet stream of a dynamic test at 200°C. The source of the trace amount of CO evolved during heating of the bound carbon adsorbent remains unknown. Gas-solid chromatographic studies show that the carbon adsorbent is selective for the adsorption of CO over N₂/O₂ (see Figure 2-20). The observed CO could be adsorbed from a laboratory source or it could be evolved due to the oxygenated surface groups on the carbon molecular sieve.

The detection of CH₂Cl₂ could be due to the halogenated organic solvents used in the laboratory. No detectable trace amounts of hydrocarbons were measured in the GC trace analyses, as described above. However, the adsorption characteristics of the carbon molecular sieve toward halogenated hydrocarbons require further study to identify the source of CH₂Cl₂ detected in the mass spectrometer.



SECTION 3

SYSTEM EVALUATION

INTRODUCTION

Equilibrium data for the CCSD-6 sorbent were used to generate preliminary system data for the purpose of comparing the characteristics of a 2-bed regenerable CO₂ removal system using carbon molecular sieve with the other techniques presently considered for a space station.

The requirements for the design of the two-bed system were these currently specified or the baseline space station atmosphere.

Total pressure: 14.7 psia
Cabin temperature: 70°F
CO₂ partial pressure: 3.0 mm Hg
CO₂ production rate: 2.25 lb/man-day
System design capacity: 3 men

Parametric system performance data were generated, but the system was no optimized for minimum weight-power penalties for the space station.

SYSTEM DESCRIPTION

A schematic of the system is presented in Figure 3-1. Process air from the cabin is circulated through the adsorbing molecular sieve bed by means of a blower. At the outlet of the blower, the air is cooled to a temperature of 50°F to enhance sorbent performance. An alternate arrangement would be to draw the process air from a location downstream of the cabin humidity condenser.

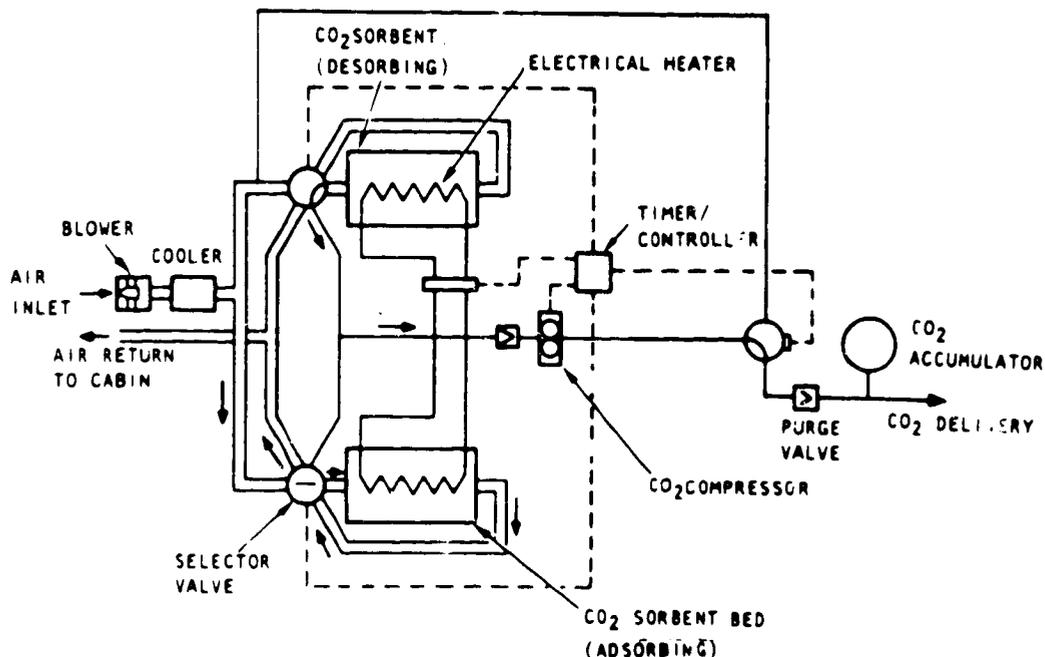


Figure 3-1. System Schematic

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While one bed is adsorbing, the other is being desorbed by heat addition. An electrical heater in the sorbent canister provides the thermal energy necessary for this purpose. The adsorption and desorption times were assumed equal with power applied to the electrical heaters for the entire desorption period. Upon switching the selector valves the air contained in the desorbing bed will be recycled to the system inlet by the CO₂ compressor. This purge process will be completed in a very short period; the oxygen and nitrogen adsorbed on the sorbent will be returned to the cabin as well as the ullage air.

Figure 3-2 illustrates the configuration of the sorbent beds with the sorbent pellets contained within the plate fin passages of the heaters. The electrical heating blankets are bonded between the brazed modules stacked to make up the complete heater. This arrangement minimizes thermal resistance between the sorbent pellets and the heater surfaces. The use of offset fins will reduce the deleterious effects of channeling.

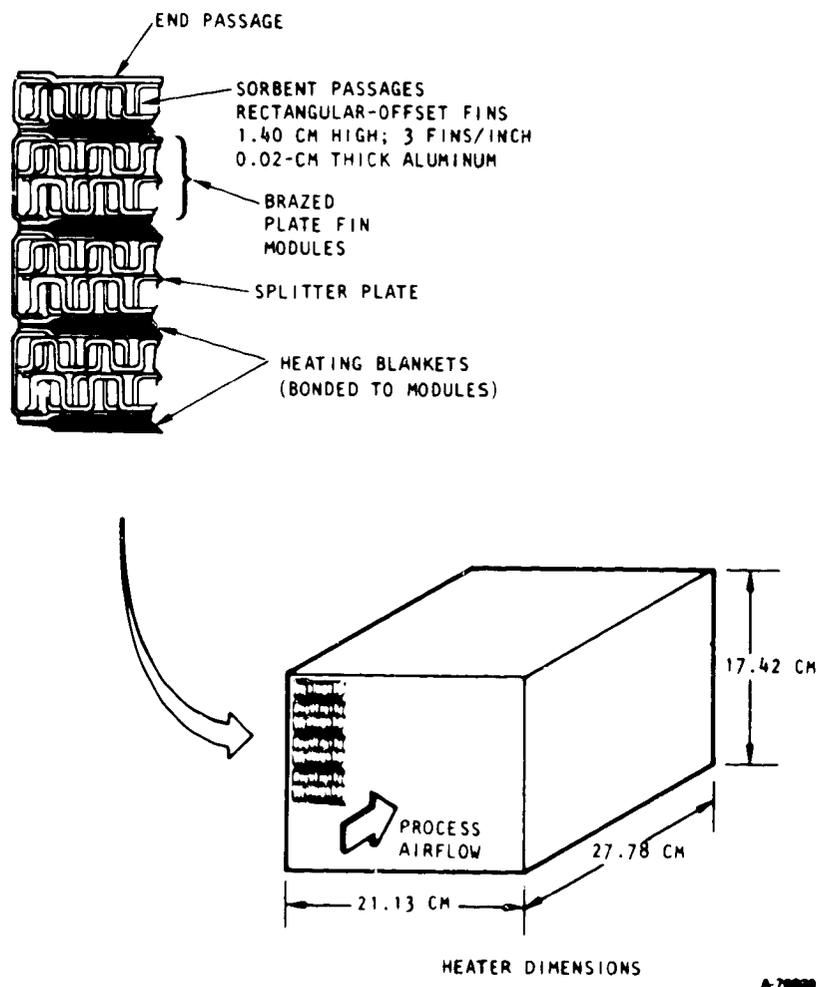


Figure 3-2. Electrical Heater Configuration

SORBENT WORKING CAPACITY

Figure 3-3 shows the CO₂ capacity of CCSD-6 plotted as a function of temperature for CO₂ partial pressures of 3 and 76 mm Hg corresponding to the pressures typical of adsorption and desorption conditions. These data were extrapolated from the equilibrium plot of Figure 2-16. Similar data for zeolite 5A also are shown on the same plot. The 3-mm-Hg pressure is the Space Station design cabin partial pressure; the 76-mm-Hg pressure was selected for desorption as a typical value attainable with a CO₂ compressor ratio of 10:1 relative to ambient. The plot shows that with a bed saturated at 10°C and 3 mm Hg about 90 percent of the CO₂ can be desorbed from CCSD-6 at a temperature of 65°C (150°F) and a pressure of 76 mm Hg. By comparison, starting with the same adsorption conditions, a temperature as high as 150°C (300°F) is necessary for desorbing only about 2/3 of the CO₂ adsorbed on zeolite 5A. Using these conditions as typical of system operation, the potential working capacity of CCSD-6 is about 0.1 g (0.1 - 0.01) CO₂ per gram of sorbent, while that of zeolite 5A is only 0.04 g (0.06 - 0.02) CO₂ per gram of sorbent as illustrated in Figure 3-3.

An important factor here is that while zeolite 5A requires temperatures on the order of 150°C (300°F) for desorption, CCSD-6 can be desorbed to a lower equilibrium capacity at temperatures as low as 65°C (150°F). This will result in power savings far exceeding those anticipated by comparison of working capacities alone. Furthermore, in a four-bed system, the thermal energy necessary for operation is determined by the requirements for desiccant

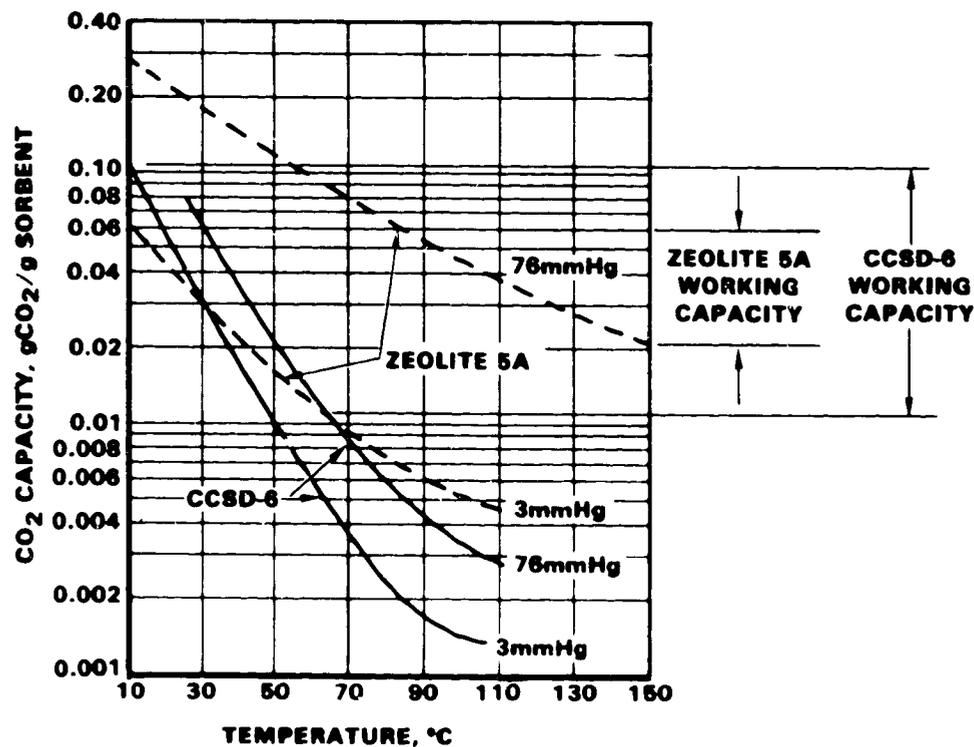


Figure 3-3. Sorbent Working Capacity



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regeneration; it follows that to provide sufficient heat to ensure adequate desiccant desorption, the CO₂ sorbent bed must be heated at about 180°C.

The equilibrium data presented were obtained on the pure sorbent without binder. Binder development reported earlier indicates that the final sorbent pellets will contain about 12 percent binder. For this reason, the capacity data of Figure 2-16 were reduced accordingly to estimate the performance of the two-bed system.

PARAMETRIC PERFORMANCE

The performance of the two-bed system is plotted in Figure 3-4 as a function of cycle time. The data were generated using AiResearch sorbent system performance prediction computer program. In this program the sorbent bed is divided into a number of thin slices (nodes) in the direction of the process air flow. Mass transfer and thermal effects are computed in each node for small time increments compatible with stability of the calculation. In this manner sorbent and process air temperature and CO₂ content are continuously calculated and the performance of each node as well as the overall bed is determined. The validity of the analytical technique and the capability of the program to predict test performance has been established during the development of the Skylab RCRS.

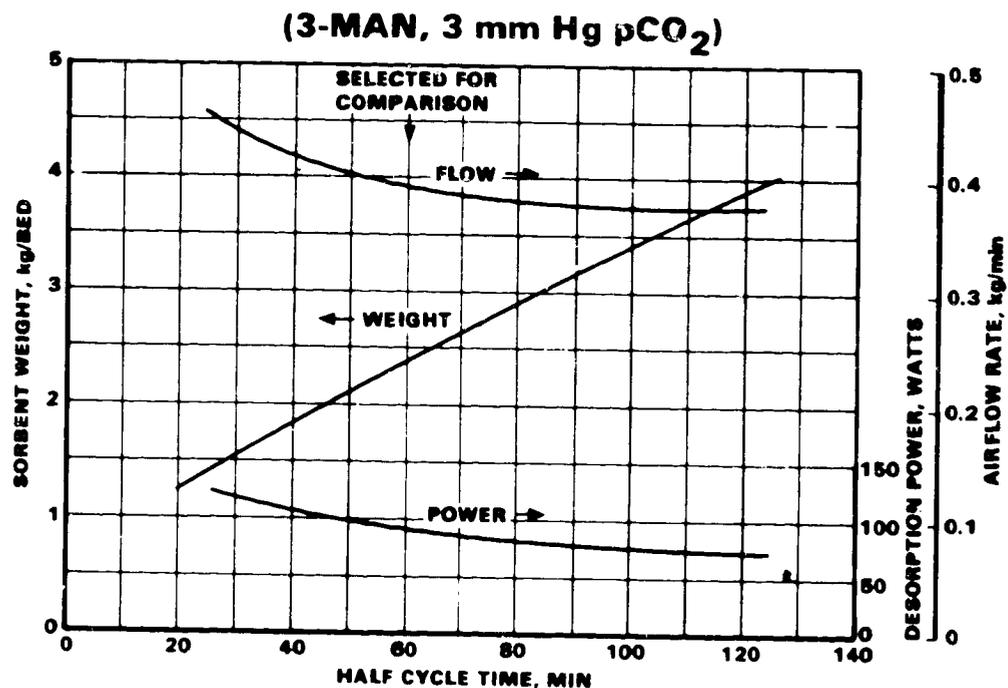


Figure 3-4. System Parametric Data

The effect of desorption temperature was not evaluated. A value of 74°C (165°F) was used. Referring to Figure 3-3 the sorbent working capacity gained by increasing desorption temperature from 65° to 74°C is less than 3 percent while the desorption power is increased by about 15 percent. The 74°C desorption temperature used for preliminary evaluation is very conservative; a lower desorption temperature assumption would result in reduced power estimates.

The shapes of the weight and power curves on Figure 3-4 reflect the rapid cooling of the carbon molecular sieve bed at the start of the adsorption cycles; the effective bed temperature drops rapidly from the 74°C (165°F) level and, about 6 minutes into the cycle, the bed starts adsorbing. By comparison, a zeolite 5A bed desorbed at 182°C (360°F) will not adsorb CO₂ before about 25 minutes into the cycle. As a result, sorbent weight is nearly proportional to cycle time and the desorption power curve is relatively flat. The longer cycle time does not result in significant power savings.

For purposes of comparison, a 60-min half-cycle time was selected. Shorter cycle times may be optimum if the power penalties are lower than about 400 lb/kw.

COMPARISON OF APPROACHES

The data of Figure 3-4 were used to compare a two-bed carbon molecular sieve CO₂ removal system with the three major contenders for space station:

- (a) Four-bed zeolite molecular sieve system
- (b) Solid amine water desorbed system (SAWD)
- (c) Electrodepolarized cell system (EDC)

The four-bed zeolite system represents the state-of-the-art for CO₂ removal, and the no-risk approach. Estimates of the characteristics of a 4-bed zeolite system and of a two-bed carbon molecular sieve system are presented in Table 3-1 for 45- and 60-minute half-cycle times. In all cases, the desorption period was the same as the adsorption period. All systems shown include a blower, a CO₂ compressor, and a CO₂ accumulator as shown in Figure 3-1 for the two-bed case.

These data are conclusive. The two-bed approach is about half the weight and power of the four-bed system. Other system arrangements could be used to further reduce the two-bed system penalty. As an example, an external heater could be used and carbon dioxide could be circulated in a closed loop around the external heater and the desorbing bed to transport to the sorbent the thermal energy necessary for desorption. Such an arrangement would reduce heater power by as much as 30 percent. The electrical heaters in the sorbent beds would be eliminated; however, additional hardware would be required for CO₂ flow control.

Table 3-2 is a comparison of the two-bed system (60-min half cycle time) with the other approaches. The advantages of the two-bed approach are clear. Weight is considerably lower, so is power. In terms of durability, this type of system has been demonstrated on Skylab. Some of the critical hardware, namely the system selector valves and electrical heaters could be the same design as used on Skylab. These valves have been subjected to extensive life tests, corresponding to about one year of operation on space station.



TABLE 3-1
 ZEOLITE/CCSD-6 SORBENT SYSTEM COMPARISON
 (3-MAN CAPACITY AT 3.0 mm Hg PCO₂)

Parameter	4-Bed Zeolite		2-Bed CCSD-6	
Half Cycle Time, min	45	60	45	60
CO ₂ Sorbent, kg	6.6	8.2	3.5	4.8
Desiccant, kg	9.2	11.3	-	-
Desorption Temp., °C	182	182	74	74
Airflow, kg/min	1.2	1.05	0.43	0.39
System Weight, kg	78.5	87.9	44.1	48.1
Heater Power, w	379	352	81	92
Total Power, w	566	535	216	230

TABLE 3-2
 COMPARISON WITH COMPETING APPROACHES
 (3-MAN SYSTEM; 3.0 mm Hg PCO₂)

Parameter	2-Bed CCSD-6	4-Bed Zeolite	EDC	SAWD
Weight, kg	48.1	87.9	76	99
Volume, m ³	0.26	0.33	0.27	0.35
Power, w	230	535	344	511

A two-bed carbon molecular sieve system is clearly superior to all competing systems presently considered for space station.



SECTION 4
CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

A number of carbon molecular sieves have been synthesized and evaluated for CO₂ removal from air at partial pressure of 0.4 kPa. The program has been very successful and all program objectives have been met. Significant achievements and major conclusions are summarized below.

- Many sorbent materials have been prepared which offer potential for CO₂ removal on space station.
- More than 90 sorbent preparations have been produced representing 39 different carbon molecular sieves.
- Of the eight starting polymers used as precursors, five have been identified as promising. The polyvinylidene chloride-polyvinyl chloride copolymer produces carbons with the highest CO₂ capacity. The formulation of this polymer is critical in the preparation of the carbon adsorbent. A polyvinylidene chloride homopolymer appears to be the best substitute but yields a molecular sieve of reduced capacity.
- A combination of petroleum asphaltene and sulfite pulp waste liquor has been developed as suitable binder. A minimum of 12 percent binder is necessary to provide adequate mechanical strength for the adsorbent pellets. Limited dynamic breakthrough tests showed that the binder does not adsorb CO₂. Binder development should be emphasized in any follow-up program.

Adsorption capacity for carbon dioxide in the partial pressure range of interest is more than adequate.

- CO₂ capacities in the range of 0.011 to 0.033 g/g-sorbent have been measured at room temperature and CO₂ partial pressure of 0.5 kPa.
- The carbon molecular sieve equilibrium curves are much shallower than those of zeolite sorbents, indicative of reduced binding energy between CO₂ and the sorbent.
- Because of lower binding energy, the carbon molecular sieve has been found to desorb CO₂ at temperatures significantly lower than that for 5A zeolite.
- The available working capacity of the carbon molecular sieve selected for comparison is twice that of the zeolite sorbents.



Carbon molecular sieves have been found to be selective for CO₂ over moisture under dynamic coadsorption conditions. Under static conditions, water adsorption on these carbon adsorbents at relative humidities lower than 50 percent is negligible. Adsorption of water is very slow and the amount of water adsorbed at relative humidity higher than 50 percent is strongly affected by the synthesis conditions of the adsorbent.

Material stability has been demonstrated. Gas mixtures collected from the dynamic breakthrough tests at 200°C show no detectable contaminants.

Sufficient data were generated to permit a meaningful characterization of a 2-bed regenerable system for CO₂ removal on space station. Equilibrium data generated over a range of temperature were used to develop parametric data and preliminary estimates of weight, size and power. These data are believed to be conservative.

The two-bed molecular sieve system offers significant weight and power advantages over all competing CO₂ removal approaches. The weight and power of this novel system are about 1/2 to 3/4 that of the 4-bed zeolite molecular sieve system, the solid amine system and the electrodeposited cell.

The system data are preliminary in nature but the advantages are of such a magnitude that the same conclusions would be reached even if the estimates of sorbent bed weight and desorption power were in error by more than 50 percent. Sorbent bed performance data used analytical tools developed for the Skylab RCRS program. Hardware weights were derived largely from RCRS data. It follows that the 2-bed system data presented are realistic based on conservative assumptions made in selection of system operating parameters, (viz. desorption temperature and cycle time).

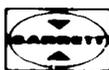
RECOMMENDATIONS

The development of carbon molecular sieve for CO₂ removal on space station was initiated in June 1985. The results of this six-month feasibility program have surpassed expectations. Sufficient data have been generated to determine with confidence that a 2-bed carbon molecular sieve system using this material is far superior in terms of weight, power and development risk to other CO₂ removal concepts considered for space station. On the basis of these data, AiResearch recommends that the two-bed system be adopted as the baseline for the initial space station environmental control and life support system configuration.

Enough time is available to permit system demonstration in 1986. The go-forward program will include two concurrent activities:

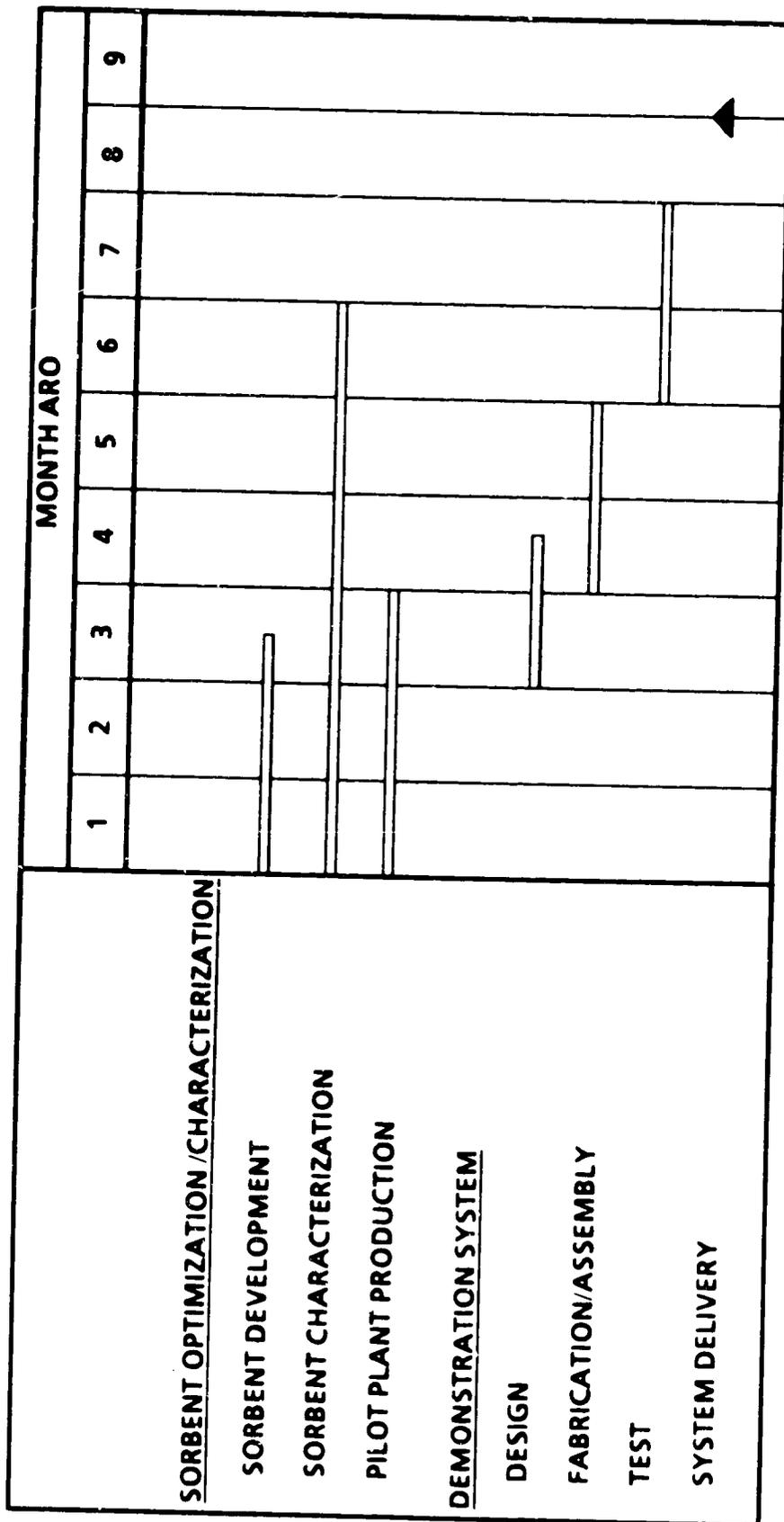
- (a) Sorbent optimization/characterization
- (b) Demonstration system development

Figure 4-1 shows the program schedule.





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Figure 4-1. Recommended Program Schedule

Sorbent Optimization/Characterization

This is a continuation of the initial effort. The objectives of this task are to 1) optimize the sorbent material itself in terms of preparation and capacity, 2) fully characterize the sorbent to permit accurate bed sizing and 3) develop production procedures suitable to support the demonstration program. This task can be accomplished in a 6-month period and will include the following activities.

(a) Sorbent Development

- Starting polymer optimization
- Optimization of preparation procedures
- Complete binder development
- Sorbent selection

(b) Sorbent Characterization

- Complete CO₂ isotherm map
- H₂O isotherms
- Dynamic coadsorption
- Stability evaluation

(c) Production Development Pilot Plant

- Sorbent material
- Binder
- Pellets

System Demonstration Effort

The system demonstration effort constitutes the second major task of the go-forward program. This effort will also extend over a 6-month period and result in delivery of a system to NASA for long term demonstration following development.

This system could be assembly with RCRS hardware including canisters, sorbent electrical heaters, valves and controls. This approach was assumed in developing the schedule of Figure 4-1.



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